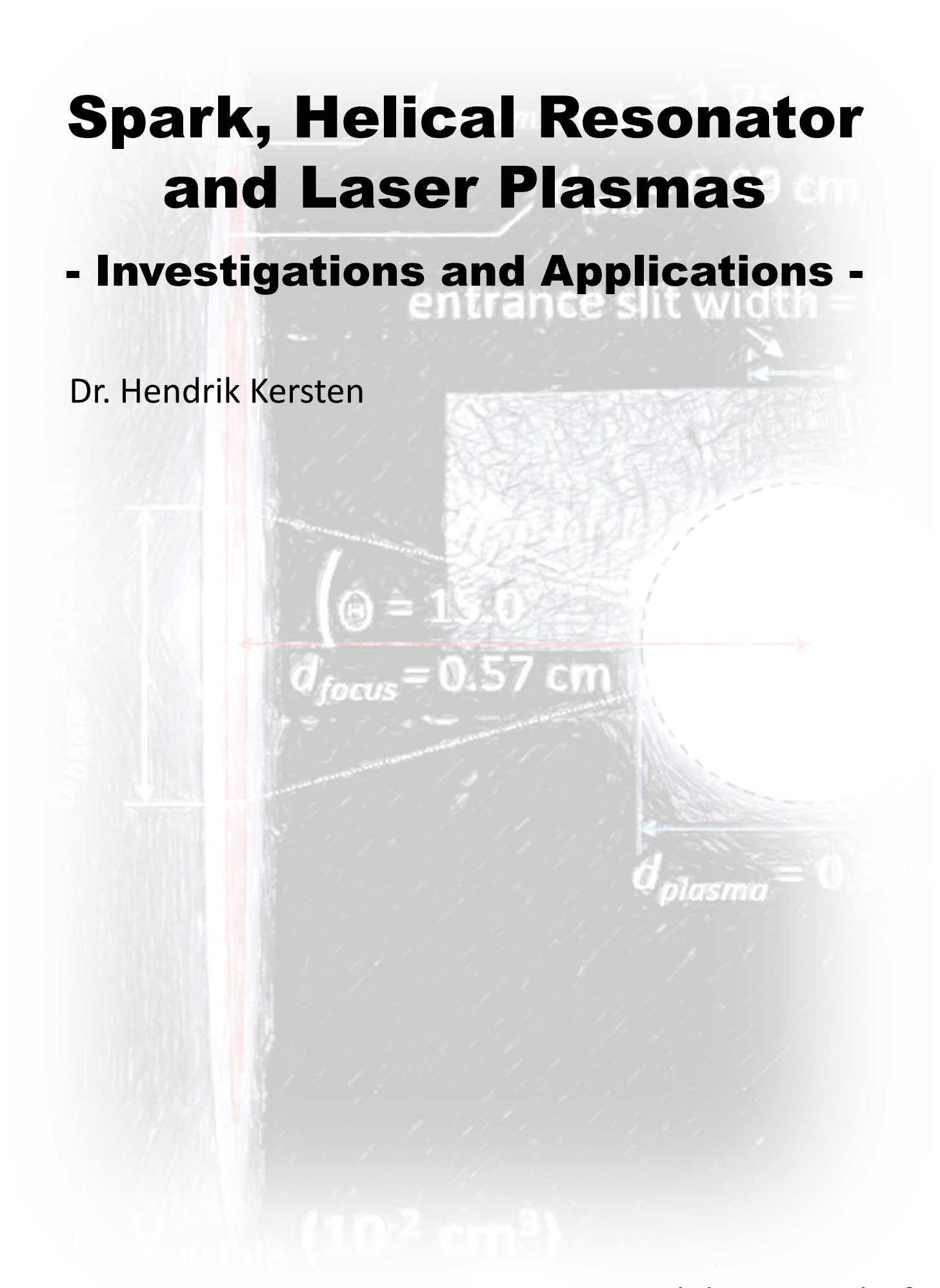


Spark, Helical Resonator and Laser Plasmas

- Investigations and Applications -

Dr. Hendrik Kersten



Thank You

To all of you that have contributed to this work - and there are many: Thank you so much.

To Klaus, Ian and Faezeh: You left this world too early.

To Josche, Aenne and Kalle: You are awesome. I love you. *“Don't let their fears make you afraid”*
(*Bastards, Machine Head*)

To Elena: This one is for you. Took me some time, but here it is. I could not have done it without you.
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I GENERAL INTRODUCTION

1 The Fourth State of Matter

The fourth state is a fascinating condition of matter, well-known for its characteristic, iridescent and colorful luminescence. It is quite remarkable that it contributes more than 99 % to the visible matter in the universe, though on earth the states solid, liquid and gas are much more familiar to us. Whether plasmas are large or small, hot or cold, dense or rarefied, they all share one common key feature: The content of sufficient energy for the coexistence of liberated electrons and positive ions within a defined volume. The resulting collective behavior of the charge carrying species - the reason for calling it a state of matter - leads to unique plasma properties such as the specific and beautiful emission of light, the response to electrical and magnetic fields with distinct current/voltage characteristics and/or the formation of chemically reactive species. All these typical plasma properties impart unique features to many practical everyday life applications (e.g., plasma monitors, fluorescent lamps) and to vast industrial processes such as surface treatment or coating techniques in the semiconductor manufacturing sector, just to name a few.

Plasmas are highly dynamic systems with a multitude of simultaneously running processes on sometimes largely differing time-scales. An almost endless number of possible (excited) species - each with their own specific reactivity -, the collective behavior due to the strong Coulomb forces between charged particles, energy distributions mostly far from equilibrium, and the intertwined interaction of radiation

with species from the plasma volume and the chamber walls - all these make this state of matter difficult to handle, but surely unleash its fascination for research. The key challenge lies in optimizing the plasma conditions in terms of energy input, gas density and composition, and balancing various loss mechanisms, just to name a few. This meticulous control is needed to ensure the plasma generates the most favorable combination of the specific chemical species, radiation, kinetic energies of bombarding particles and so forth, tailored to whatever is required for the specific application.

The aforementioned plasma properties also enable its investigation through various methods. Spectroscopic analysis of their emitted radiation is a primary approach, providing valuable insights into the energy distribution within the plasma. However, a key limitation lies in the accessible wavelength range per experimental setup. Each spectral region necessitates specific conditions, rendering the acquisition of a vacuum ultraviolet spectrum vastly different from one in the visible or infrared range. The charged nature of plasmas allows for voltage, current, and charge density measurements. These measurements, among other things, offer information on the ionization state of the plasma species. By incorporating time-resolved techniques into these various methods, plasma researchers gain a comprehensive understanding of the plasma's dynamic behavior, encompassing both its physical and chemical processes.

Mass spectrometry, a further cornerstone of the author's research, plays a particularly significant role related to plasmas. In 1897, J.J. Thomson used plasmas to revolutionize the most fundamental concept of our modern view on matter [1] and was deservedly rewarded the Nobel Prize in 1906. Based on his brilliant experiments he concluded that different atomic and molecular gases are made of one and the same negatively charged elementary "corpuscles", nowadays known as "electrons". For Thomson, plasmas acted like "nutcrackers", providing sufficient energy to eventually break atoms apart - the hitherto believed most elementary particles. With a combination of electrostatic and magnetic fields he was able to fairly well determine the mass to charge ratio m/z of those newly discovered subatomic units. A couple of years later, a modification of his experimental setup allowed for the investigation of the positively charged gas-phase particles as well. Those experiments revealed the existence of hitherto unknown isotopes and revolutionized our picture of the subatomic structure once again. In general, Thomson's instrument measured the mass-to-charge ratio m/z and with known charge, simply identified any atom or molecule by its mass. This concept of a "mass spectrometer" has gained much popularity over the last century and the technique has developed into high-tech machines, indispensable for modern laboratories whenever molecular information, even far beyond the mere mass, is needed. Nowadays user-friendly mass spectrometers off-the-shelf are firmly integrated in particular into areas issuing food, environmental-, process- and bioanalytical applications. Despite the progress in all the

technical refinement of modern mass spectrometers, still today plasmas play a major role as “nutcrackers” to provide a charge for a mass so the machine can eventually measure the fundamental quantity m/z , just as in the early experiments in Thomson’s lab. Vice versa, mass spectrometers are important diagnostic tools for plasmas themselves. Hence, mass spectrometry and the field of plasma research remain closely intertwined.

2 Present Work – DFG Grant, Subsequent Projects and General Progress

The present work introduces and summarizes a selection of the author’s projects of the past twelve years, addressing fundamental aspects of plasmas, some in close relation to mass spectrometry. It was initiated by a German Research Foundation (DFG) grant in 2012 [2], which involved the fundamental investigation of a miniaturized spark discharge light source, awarding 435 000 € to the author. It allowed the development of essential equipment and establish the field of “*Plasma Research*” in the Physical and Theoretical Chemistry group at the University of Wuppertal. Several research projects with companies and other institutes followed, adding another 130 000 €, in addition to instrument and hardware donations. Research that involved the work of six PhD students, seven master- and eight bachelor students will be presented. Their scientific output is the basis of 20 poster presentations, 11 peer reviewed articles, two commercialized products, the initiation of a spectral database, four talks on international conferences and two filed patents.

Our perception by the community in this realm also lead to the author’s invitation as a session chair and discussion leader on two international conferences (i) Gordon Research Conference in 2016, “Plasmas with Complex Interactions - Exploiting the Non-Equilibrium” in Andover, NH, USA and (ii) 67th ASMS Conference on Mass Spectrometry and Allied Topics in 2019, “Fundamentals: Photoionization and Photodissociation” in Atlanta, GA, USA. In 2021, the author co-authored a successful research proposal for a DFG instrument (ICP-MS) grant awarded to the University of Wuppertal. Our contribution focused on fundamental research on the inductively coupled plasma (ICP). The proposal involved collaboration with the Food Chemistry Department (Prof. Dr. Bornhorst) and the School of Architecture and Civil Engineering (Prof. Dr. Rinklebe), as the application lead. Since May 2023, the author is actively involved in the EU-project 14AMI (14 Angstroms Module Integration) within the HORIZON-KDT-JU-2022 call. Together with 30 internationally renowned partners from the semiconductor sector a total funding of 25 M€ has been approved, with our group being funded with 534 000 € over the next three years. Our contribution is the investigation of pulsed extreme ultraviolet (EUV) induced plasmas. In this realm a further company from the semiconductor industry field

supports our work with further 1.25 M€ for the period 2021 to 2026, which was also noted in a local newspaper article¹. This latter research project represents our current primary focus, involving a team of seven PhD students and two postdoctoral researchers under the author's guidance. However, this is not subject to the present writing. Furthermore, in his capacity as a lecturer for physical and theoretical chemistry courses at the bachelor's and master's levels, the author introduced a new module in the chemistry master's program in 2018. This module, consisting of two lectures and a laboratory course, focuses on the fundamentals of mass spectrometry and ion mobility, also with a strong emphasis on the underlying principles of plasmas. This addition has become a valuable part of the overall chemistry master's curriculum at the University of Wuppertal.

Following this introductory chapter I, this work is organized into three main chapters, each focusing on research conducted with a specific type of plasma: II SPARK PLASMA, III HELICAL RESONATOR PLASMA, and IV LASER PLASMA. Each chapter begins with an abstract, providing a general overview of the type and research conducted with that specific plasma family. The abstract is followed by an introduction to the topic, a detailed presentation and discussion of the research results, and a concluding section that summarizes the key takeaways and outlines future directions.

The reader may notice the use of the pronouns "our" and "we," which clearly highlight the collaborative nature of this work. Each contributor will be acknowledged by name in the respective chapter.

I hope the reader enjoys reading this work.

Hendrik Kersten

Wuppertal, December 2, 2024

¹ https://www.wuppertaler-rundschau.de/lokales/bergische-uni-foerderung-im-bereich-der-halbleiterfertigung_aid-65037391

II SPARK PLASMA

1 Abstract

Fundamental as well as application driven investigations of a unique spark type initiated the independent field of *Plasma Research* within the research structure of the Physical and Theoretical Chemistry group at the University of Wuppertal. This particular plasma brought forth a German Research Foundation (DFG) grant [2], two filed patents [3, 4] and the initiation of a spectroscopic online database [5]. In addition, it generated a scientific output of two master theses [6, 7], three bachelor theses [8-10] and eight poster presentations on international conferences [11-18]. Unfortunately, due to personal circumstances, one PhD student in that project had to discontinue research in this area.

Motivated by the need for a spatially tightly confined and bright photoionization source we developed a miniature spark discharge. A tube-type electrode assembly with half a millimeter radius and a spark length of about one millimeter, was built into an analyte gas flow conducting glass capillary of a mass spectrometer. Though the orifice between the plasma region and the analyte gas stream was as small as 0.1 mm^2 , this spark discharge generated photoionization rates comparable to conventional plasma lamps that illuminate two orders of magnitude larger areas. This unique miniaturized assembly significantly reduced the power supply requirements and any electronic interferences with peripheral equipment, which is most often a criterion for excluding spark plasmas from practical applications.

Propelled by these encouraging results we applied for funding to further investigate the fundamental characteristics of this particular spark type. In 2012 the DFG granted a three year funded project with a one year extension to the author. During this time we systematically investigated the impact of the electrode shape and the discharge gas pressure, flow and composition, with a focus on (i) the temporal and spatial plasma stability, (ii) the temporal profile of the discharge current, voltage and light emission, and (iii) the spectroscopically resolved radiation between 40–1 200 nm. The latter turned out to be a valuable tool to link the ultraviolet (UV), visible (VIS) and near-infrared (NIR) spectral region with the experimental more demanding vacuum-ultraviolet (VUV) range of emitted photons. Consequently, we set up an online database to make these results publicly available. Of particular interest was the VUV emission of the helium dimer (He_2^*), centered around 82 nm. Several exciting experiments were carried out to reveal its chemistry with respect to pressure dependency between 400 mbar and 1 500 mbar and quenching effects with different additives. Based on the concept of appearance energy determinations with a mass spectrometer, we attempted to follow the dimer forming metastable species. However, to date this effort was not successful. Recent experiments demonstrated the functionality of the spark source in liquid nitrogen, which will be an interesting medium for prospective fundamental research.

Its small design, low power requirements, wide pressure range and its efficiency in particular at high pressures, render this mini spark source appealing for various applications. Concepts for (i) a metal aerosol sampling and ionization device, (ii) an alternative to the helical resonator plasma source (cf. chapter III HELICAL RESONATOR) and (iii) a capillary electro-kinetically separation (CESE) technique were designed, built and tested [19].

2 Introduction and Theory

Since 2009 we investigate the effects of ion chemistry in modern atmospheric pressure ionization mass spectrometers (API-MS) [20]. In 2011 the strong impact of post ionization processes during a kinetic degradation study of atmospherically relevant compounds was demonstrated [21]. In these studies, the compound of interest is introduced into a large chamber with synthetic air at mixing ratios of around one ppmV. Consecutive oxidation processes with hydroxy radicals, oxygen and nitrous oxides degrade these precursors. The concentration-time profiles are monitored with various analytical tools in order to obtain rate constants for the degradation process and the formation of products. We showed that monitoring results with an API-MS instrument can severely misrepresent these concentration-time profiles caused by a rich, superimposed ion chemistry. Essentially, the titration of the precursor ion population by a neutral degradation product

resulted in a much faster degradation and rendered the deduced rate constants largely incorrect. Hereupon, we introduced the field of *capillary atmospheric pressure ionization* (cAPI), aiming at a reduced and, to a certain limit, controlled amount of reactive ion-molecule collisions [21, 22]. The general concept pursues the implementation of ionization methods in the near supersonic flow of capillary conducts that separate the atmospheric from the first differential pressure region of API-MS instruments. In depth studies describing the fluid dynamics and the choked flow conditions in these half-millimeter channels followed [23]. Furthermore, new concepts of ionization were required to ensure efficient and stable ion generation in these rather restricted dimensions. One of the first realized cAPI designs used a miniature spark discharge for a spatially confined but bright photoionization source. A tube-type electrode assembly of half a millimeter radius and a spark length of less than a millimeter was built on top of the analyte gas flow conducting glass capillary of a mass spectrometer (cf. Figure 1) [21]. Although the orifice between the plasma region and the sample gas to the MS was as small as 0.1 mm^2 , this spark discharge generated photoionization rates comparable to conventional plasma lamps that illuminate two orders of magnitude larger areas [24]. Typically, an argon flow of around 300 sccm was provided through the anode and actively pumped through the cathode. A switch-mode power supply (custom configured DD20_10 C-Lader, Hartlauer Präzisions Elektronik GmbH, Uebersee, Germany) repeatedly charged two capacitors (1 nF each) up to +1 500 V with a frequency of 1 500 Hz. In short-circuited operation mode, this charging process is regulated by the breakdown voltage, which in turn is a function of the characteristic lamp setup and its general operating conditions (electrode distance, shape, material, gas type and gas pressure).

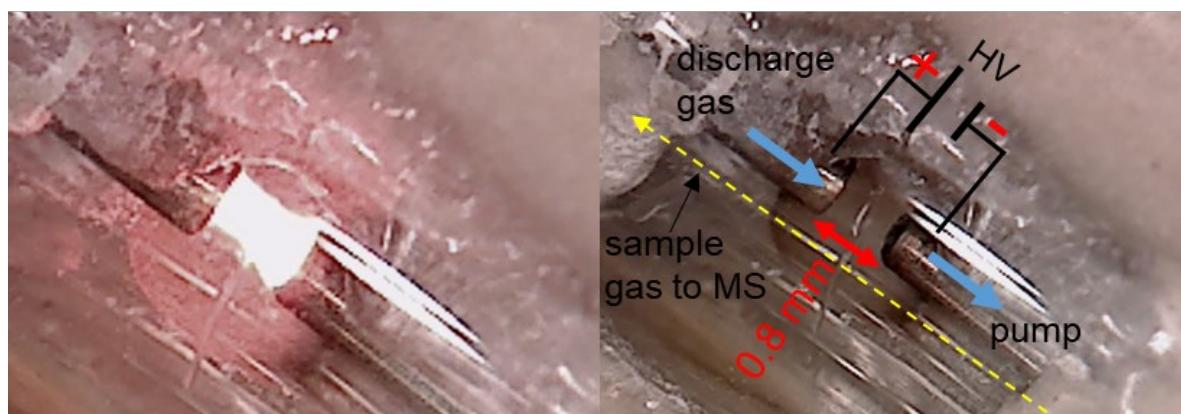


Figure 1: Spark assembly of tube-type electrodes, built on top of the conduct of a glass capillary in a mass spectrometer.

Figure 1 shows an enlarged picture of the cylindrical plasma evenly centered between the electrodes and exactly matching the conduct of the analyte guiding glass capillary. This unique miniaturized assembly generated spatially and temporally stable discharges and it significantly reduced the power supply requirements to prevent electronic interferences with peripheral equipment. Criteria that most often exclude sparks in

certain practical applications. From an analytical perspective this ionization device, in combination with an ion-trap mass spectrometer, provided limits of detection down to 100 pptV [24] and clearly demonstrated the reduction of distorting ion molecule reactions [21].

2.1 Sparking Theory

A look at the underlying plasma mechanism reveals fundamental similarities to the natural lightning. In the mid-18th century, Benjamin Franklin demonstrated with his historical kite experiment that electrical charges are the cause of these beautiful as well as frightening phenomena. At that time, laboratory experiments with static electricity were well known. However, it took around 200 years after this initial experiment to answer the basic question on how such an impressive amount of charge can bridge a normally non-conducting air gap within fractions of a second. This breakthrough of high current pulses in incredibly short time intervals is the most prominent characteristic that spark plasmas and lightning share in common. In particular the works of Loeb, Meek, Schonland, Raizer and Komelkov [25-34] significantly contributed to our present understanding of short-circuiting in high-pressure gaseous insulators.

What about the assembly shown in Figure 1? Here the power supply charges two capacitors to establish an electrical field between the electrodes with increasing field strength. At a certain limit, however, the electrons instantaneously leave the lower electrode (cathode), proceed through the gas against the flow direction to the anode and leave behind the characteristic visible plasma region. This continues for several microseconds, until the capacitors are completely discharged and the electrical field is removed in a self-terminating manner. Now the setup is ready for the next charging event, which repeats with a frequency of 1 500 Hz. Several questions may arise, among others: Why do the electrons leave the cathode at a certain limit of electrical field strength? Why do the involved processes gain a momentum on their own, which makes this short-circuit seemingly unstoppable?

To find the answers, we begin with the basic electron avalanche and its multiplication in a general DC discharge, which John Sealy Townsend discovered at the end of the 19th century. We will discuss this theory in detail, since the underlying elementary principles are applicable to nearly all discharge phenomena. A profound understanding of these few principles greatly aids to derive qualitative pictures of the very different DC plasma modes and even for the manifold of RF plasmas.

2.1.1 Townsend Discharge

Consider a plane electrode configuration with a gap distance d [cm] filled with some gas of pressure p [mbar] and an uniform electrical field E [V·cm⁻¹] applied through the voltage U [V](cf. Figure 2(a)). So we have the simple relation

$$E = \frac{U}{d} \quad (1)$$

Between the anode and the voltage supply, an electrometer displays the number of negative charges arriving at the anode per time (current i). Now suppose initial electrons inside the gap, liberated either from gas molecules or the cathode surface by cosmic rays or natural radioactivity. At low electrical field strength, these initial electrons slowly move towards the anode, encounter some elastic collisions with the background gas and cause a more or less constant initial current i_0 at the electrometer. Hence, this current is basically determined by the rate of the naturally occurring ionization events. This effect is illustrated in the typical voltage/current characteristic of a general DC-plasma evolution in Figure 2(b). At the lowest current, the voltage can be readily increased by a factor between 0 and U_A without noticeable change in i_0 . In this range of U , only the rate of the naturally occurring electron liberation determines the number of available electrons and these random events obviously do not depend on any applied electrical field. In air at atmospheric pressure, the initial current density is of the order of 10^{-18} A·cm⁻² [35]. A common way to deliberately increase i_0 is by simply irradiating the cathode surface with electromagnetic radiation energy above its work function.

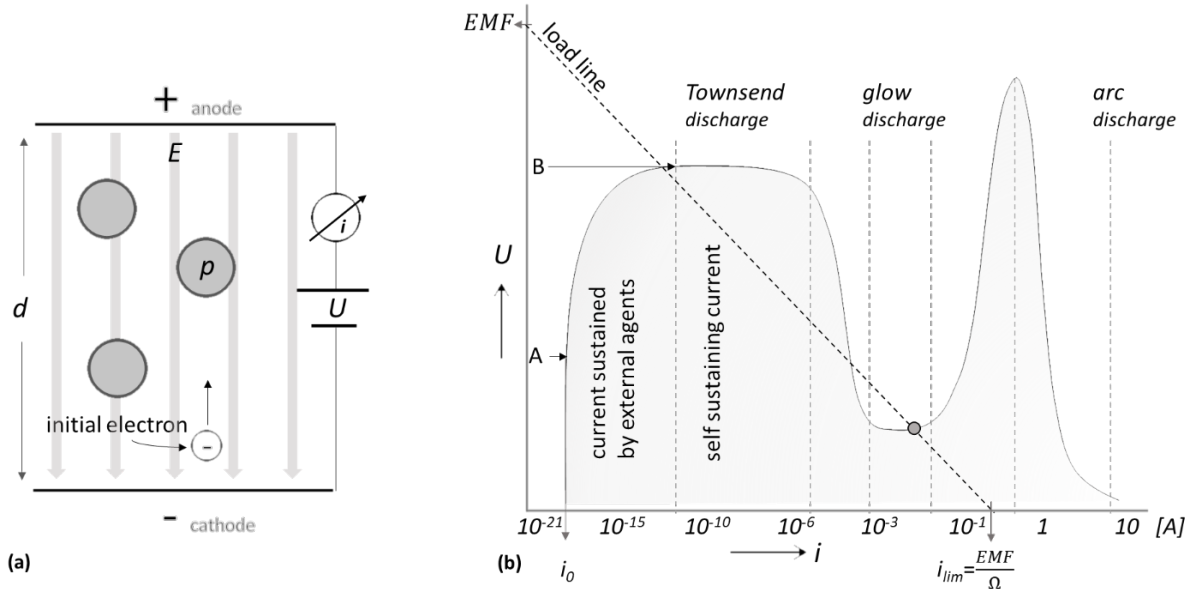


Figure 2: (a) Illustration of a plane electrode configuration to explain DC discharge phenomena and (b) typical voltage/current characteristics for a gas in a uniform electrical field - adapted from fig. 1 in [35]. Note, the current axis is of logarithmic scale only between 0.1 and 10 A.

2.1.1.1 Primary Amplification

A gradual increase in the applied voltage will cause these initial electrons to move with a higher kinetic energy. Partially, this newly gained energy will be lost in elastic collisions. On the average, however, the electrons will speed up along their mean free path λ and consequently deliver more and more energy into the collisions with the background gas. The quantity which is proportional to the mean energy of an electron at a given electrical field strength E [$\text{V}\cdot\text{cm}^{-1}$] and a given gas density n [cm^{-3}] is the reduced field strength E_r

$$E_r = \frac{E}{n} \quad (2)$$

often expressed in units of 1 Td (*Townsend*) = $10^{-17} \text{ V}\cdot\text{cm}^2$. We can also rewrite this equation in terms of the pressure, since the gas density is proportional to the pressure at a given temperature T [K] by simply the factor $(k_B T)^{-1}$, with k_B the Boltzmann constant. Thus, in combination with equation (1) we obtain

$$E_r = \frac{U}{pd} \quad (3)$$

At some point, this mean energy will be sufficient for inelastic collisions with the background gas. For the moment, only electron ionization and electronic excitation are considered as plasma relevant inelastic events. The impact of rotational and vibrational excitation will be discussed further below. Since an electron has fully exploited the potential energy of the field only after the entire passage through the gap, these inelastic processes will very likely occur at the anode first and then expand, with growing electrical field strength, all the way to the cathode. Consequently, at very low electrical field strength, the first electron ionization events are expected near the anode, which locally generate some extra electrons and add to the initial current i_0 to slightly increase the electrometer output i . The onset of this process is marked as U_A in Figure 2(b). With increasing voltage - up to U_B - these first ionization events advance towards the cathode. This also increases the probability for the newly formed electrons to gain enough energy from the field in order to produce a third, fourth and so on generation of additional electrons. This multiplication, originating from one initial electron, is called a *single avalanche process* and is schematically shown in Figure 3(a). The number of N_l electrons finally reaching the anode after a single avalanche follows a simple exponential function of the form

$$N_l = e^{\alpha \cdot d} \quad (4)$$

with d the gap distance - provided that the initial electron started at the cathode - and α [cm^{-1}], known as the first Townsend coefficient. This quantity expresses the number of ionization events per unit length and is a function of the applied electrical field, the pressure and gas specific properties such as the ionization energy IE . Townsend derived the following semi-empirical formula for this coefficient [36]

$$\alpha = Ap \cdot e^{\left(\frac{-Bpd}{U}\right)} \quad (5)$$

For most gases, even several admixtures, the specific constants A and B are found in literature as experimentally determined values [37]. Some attempts were made to calculate them on first principles as well [38].

At this point we adequately describe the exponential evolution of i in Figure 2(b) between U_A and U_B . However, no matter how much amplification we get through these single avalanches, if the formation of initial electrons stopped, the recorded current would stop as well, regardless of the applied voltage. Hence, up to U_B the current in this region is only sustained by external agents (cosmic rays, additional UV radiation on the cathode) and as soon as these are turned off, the current vanishes.

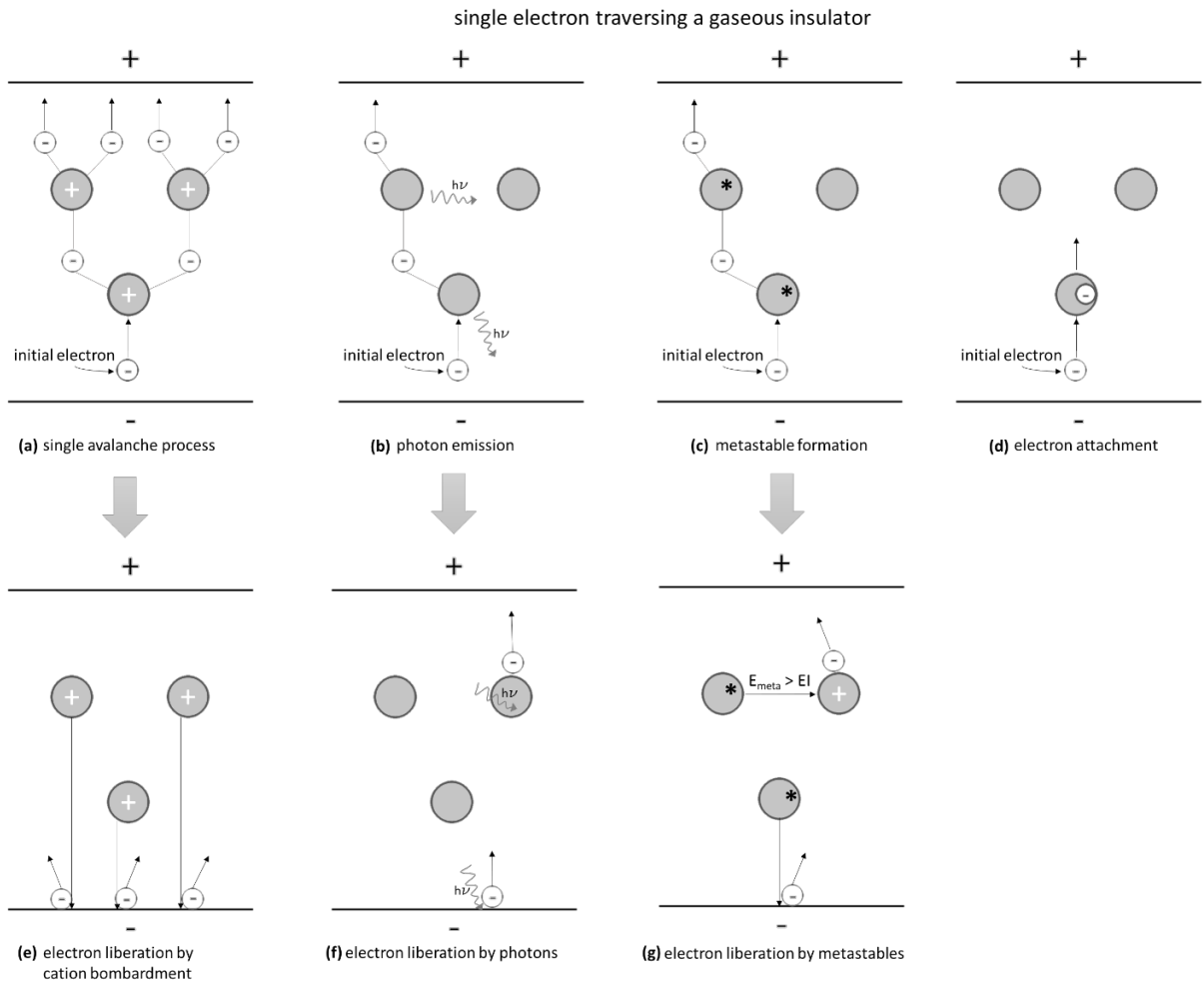


Figure 3: Illustration of the basic processes in discharges.

2.1.1.2 Secondary Amplification

Consequently, for the self-sustained discharge in the region beyond U_B , a further mechanism seems to be involved. This one must ensure that in the mean each single avalanche itself generates at least one further electron at the cathode, in order to start a

new avalanche all over again - without the aid of any external agents. When this cycle criterion is fulfilled, the external agent could be switched off and the electrometer would still show a current traversing the gas gap in the direction of the applied field, with the necessary energy provided by the power supply. Very promising candidates for releasing an electron from the cathode after each avalanche are the formed ions. Once ionized, they pick up energy from the applied field and proceed to the cathode - of course, significantly slower than the electrons moving to the opposite side. This is schematically shown in Figure 3(e). The probability for *one* ion from a previous avalanche to liberate *one* extra electron from the cathode is expressed by the coefficient γ_i and essentially depends on factors such as the field strength, pressure, cathode material, electrode geometry and surface condition. Following equation (4), *one* initial electron that passes the entire gap distance d will leave $e^{\alpha d} - 1$ positive ions behind. Accordingly, the mean number N_{II} of liberated electrons from the cathode by the cations after each avalanche, is simply this number of formed ions multiplied by their probability γ_i to knock out a cathodic electron.

$$N_{II} = \gamma_i \cdot (e^{\alpha d} - 1) \quad (6)$$

In the region up to U_B in Figure 2(b) we find $N_{II} < 1$, which means that, on the average, not every avalanche releases an extra electron from the cathode to start a new avalanche all over again. Consequently, the discharge cannot maintain itself. The point U_B exactly describes the condition of $N_{II} = 1$, at which each avalanche will, on the average, generate one subsequent avalanche. Consequently, U_B characterizes the situation of the discharge to become *self-sustained* and is thus generally referred to as the *breakdown voltage*. Sketched in Figure 3(b) and (c) are two additional fundamental mechanisms in discharges that can lead to electron liberation from the cathodic electrode, as depicted in Figure 3(f) and (g), respectively. In addition to ionization, all the field accelerated electrons in an avalanche can form electronically excited states as well, which either leads to immediate photon emission (Figure 3(b)) or in case of forbidden dipole transition states to relatively long lived metastables (Figure 3(c)). If the energy of the photon or the metastable species exceeds the work function of the electrode material, both will also be able to release an electron from the cathode when striking its surface (cf. Figure 3(f) and (g)). In the same way as with γ_i for the cations, we can assign a probability for *one* photon or *one* metastable, formed within *one* avalanche, to release *one* further electron from the cathode to start *one* successive avalanche. These probabilities are denoted γ_p and γ_m for the photon and the metastable induced liberation, respectively. We see that all three processes will contribute to the succession of avalanches to some extent, which necessitates a slight modification of equation (6). Therefore, Druyvesteyn and Penning introduced the factors N_p and N_m to normalize the number of photons and metastables *per* ion formed in one avalanche [35]. Furthermore, they introduced the geometrical factors f_p and f_m since, in contrast to the positive ion population that entirely reaches the

cathode through the electrical field, photons and metastables obviously have no such preferential field direction. With these additional factors, the following equation was derived to account for all three cathodic processes in Figure 3(e), (f) and (g).

$$\gamma = \gamma_i + (N_p f_p) \gamma_r + (N_m f_m) \gamma_m \quad (7)$$

This quantity γ is also known as the *second Townsend coefficient* and replaces γ_i in equation (6). Experimentally it is very difficult to quantify each contribution, therefore usually γ is determined as a sum parameter. Nevertheless, it is worth taking a closer look at equation (7) from a more qualitative perspective and work out conditions favoring each mechanism. Since, e.g., the probability of finding a photon from a point source in a spherical surface element scales inversely with the square of the radius, one can envision that in case of a small cathode with large distance to the anode the geometrical factor f_p will be small. On the contrary, electrode arrangements with large cathodes surrounding the anode will optimize the photon capture process and significantly increase f_p . The same is valid for metastable species. In addition, metastables can be fluid-dynamically transported into a preferred direction to increase f_m . This effect was considered in the spark assembly shown in Figure 1. Here the discharge gas is actively pumped through the gap in order to enhance the metastable induced electron liberation from the cathode.

With the factors N_p and N_m , equation (7) brings forth a further key aspect of all discharges - the electron energy balance or the answer to the question on the energy distribution among the manifold of possible states.

2.1.1.3 Electron Energy Losses

Without exception, every process in this universe is driven by energy rearrangement into the available and accessible degrees of freedom. To follow and understand a process, or a stable system comprised of a complex set of dynamic processes, we essentially need to follow the paths of potential and kinetic energy in time and space. The same holds true for discharges and plasmas. In these systems, the energy into the available degrees of freedom is primarily transported through the kinetic energy of the electrons. For a small current at low pressures, Penning derived an electron energy balance equation to determine the fractions of the energy, provided by the electrical field, distributed into elastic collisions, the overall electronic excitation, ionization, vibrational excitation of the electronic ground state and into the electron velocity increase [39]. Loss in rotational excitation is negligible [40]. Based on experimental data from literature he obtained energy loss plots for each degree of freedom as a function of the reduced field strength. Figure 4 shows a set of data points drawn from Penning's results for pure neon, a neon

mixture with 0.1 % argon, pure hydrogen and pure nitrogen. Note that these are approximated values from the original plots.

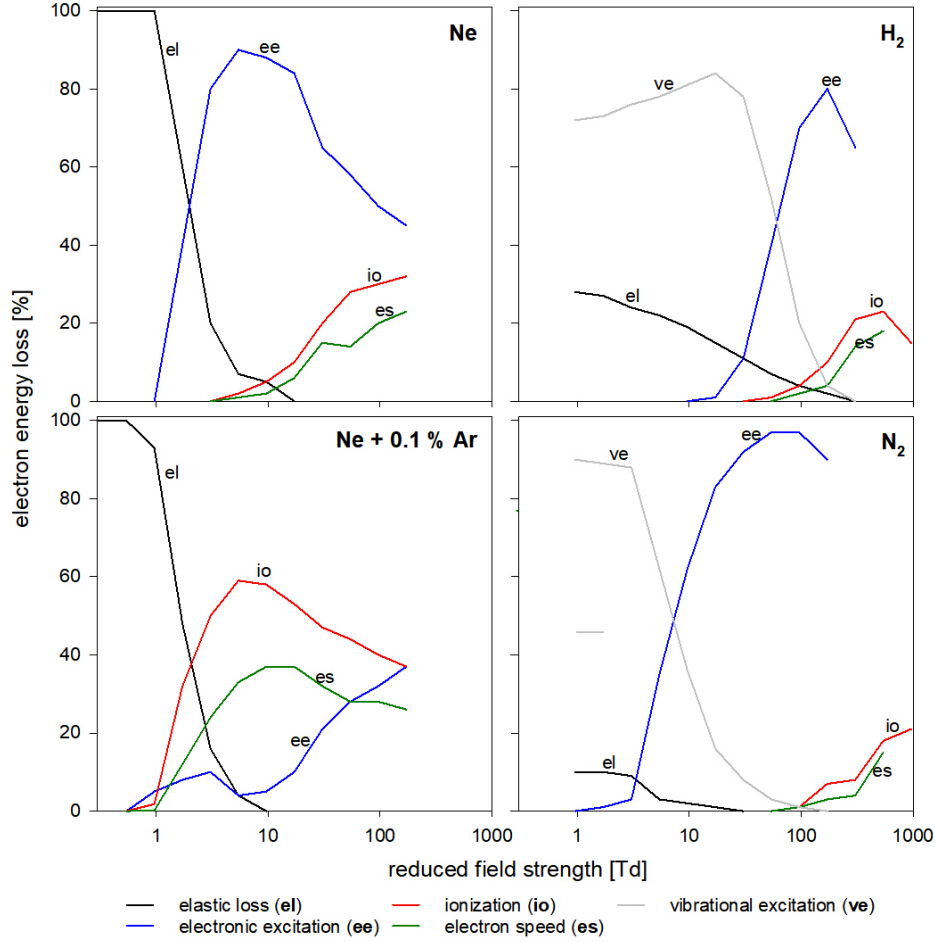


Figure 4: Fraction of the total electron energy received from the electrical field that is lost in elastic collisions, electronic excitation, ionization, vibrational excitation and increase of the electron velocity. Data points are drawn from [39] for neon, a neon-argon mixture, hydrogen and nitrogen.

2.1.1.4 Electronic Excitation, Ionization and the Effect of Impurities

These curves reveal some general interesting aspects. First of all, it is notable that in all pure gases the maximum of electronic excitation by far exceeds the maximum fraction of ionization. In neon, the latter merely reaches 35 % of the totally supplied energy and 20 % in hydrogen and nitrogen. Interestingly, in the case of 0.1 % argon addition to neon, the maximum fraction of energy branching into ionization increases up to 60 % and the electronic excitation curve shows a rather complex evolution with increasing field strength. Moreover, the onset of the ionization curve and its maximum shift to significantly lower reduced field strength. These effects are readily explained by two of the most important plasma chemistry processes, “*gas phase photoionization*” and “*Penning Ionization*”, as sketched in Figure 3(f) and Figure 3(g), respectively. The first electronic excited state of neon is at 16.6 eV [41], thus all ground state linked downward

transitions - whether radiative or not - are accompanied by energy transfer well above the ionization energy of argon at $IE_{(\text{Ar})} = 15.8 \text{ eV}$ [41]. In case of radiation, the emitted photons can cause photoionization of the argon atoms in- and also outside the electrode gap. The newly formed argon ions follow the electrical field towards the cathode and can liberate electrons to further the secondary avalanche multiplication effect described in equation (6). The same holds true for the non-radiative downward transition, the *Penning Ionization*. Here the electronically excited neon metastable population efficiently ionizes argon atoms by means of bimolecular collisions in- and outside the gap, since the condition $\epsilon(\text{Ne}^*) > IE(\text{Ar})$ is met. *Penning Ionization* thus describes a gas phase reaction, which efficiently converts electronic excitation into an increased ion population. Consequently, whenever the energy of the first electronic excited level of a neutral main gas constituent exceeds the ionization energy of a minor component, both processes - Penning and photoionization - will play a major role in nearly all plasma types. In contrast to a pure gas, the plasma will be affected in two ways: (i) Higher ion yields are obtained per avalanche and (ii) the secondary multiplication is enhanced, since previously undirected energy carrier with less capable geometry factors f_p and f_m (cf. equation (7)) now strictly follow the electric field lines towards the cathode. The latter results in an earlier self-sustained discharge and thus a shift of the breakdown voltage (point B in Figure 2(b)) to lower values. Exactly this is observed in Figure 4 for the Ne-Ar mixture: The fraction of total ionization is significantly increased and the onset of the ionization curve is shifted to lower reduced field strength. These two effects also explain the unwritten law that small amounts of impurities aid discharges in ignition and stability.

A comparison of the ionization curves in Figure 4 for the pure noble gas and the diatomic molecules, reveals a remarkable difference regarding the onset. The IE of neon is listed with 21.6 eV and thus clearly exceeds the IE s of hydrogen and nitrogen with, 15.4 eV and 15.6 eV, respectively [41]. However, the ionization of Ne already starts at around 5 Td, thus at significantly lower reduced field strength, as compared to the two molecular species. In case of H_2 the onset is calculated to approximately 50 Td and for N_2 the first ions are not formed before reaching 100 Td. As we will see in section 2.1.1.6, this also goes along with a lower breakdown voltage, viz. an earlier self-sustained discharge for neon than for the molecular species at a given set of electrode distance and pressure. At first sight this behavior seems contradictory, but is readily explained by the rather high density of accessible electronic states as the competing loss mechanism. In case of hydrogen also the excitation of vibrational states still contributes up to 50 % to the energy loss at the point of the first ionization events.

Similar arguments apply to the noticeable, rather high demand on reduced field strength for electronic excitation in the molecular system as compared to the atomic gas. Though the first excited levels of the electronic system for hydrogen and nitrogen are at 11.1 eV

and 6.1 eV, respectively, their contribution to the energy loss plot starts at significantly higher reduced field strength than for neon with the first excited level at 16.6 eV. This apparently contradicting behavior is readily explained by the large impact of the competing energy loss in the vast vibrational state density.

The factor of ten higher electronic excitation onset for hydrogen as compared to nitrogen - 10 Td vs. 1 Td - adequately reflects the 5 eV energy difference of the first electronic level.

2.1.1.5 Rotational, Vibrational Excitation and Electron Attachment

Swarm experiments and supportive calculations showed the fractional energy loss for rotation to be negligible for electron energies above the first excited vibrational level [40], which are at 0.5 and 0.3 eV for hydrogen and nitrogen, respectively. Therefore, rotational excitation by means of partially converting the kinetic energy of the electrons, only competes with the elastic loss process of slow electrons at nearly thermal energies. Accordingly, the rotational contribution is not considered in Figure 4.

The electron energy loss based on vibrational excitation, however, is significant. For hydrogen the fractional contribution is around 75 % at 1 Td and still around 20 % at 100 Td (cf. Figure 4). Due to the 0.2 eV lower first excited vibrational energy level of nitrogen, the loss in this degree of freedom even makes up to 90 % at 1 Td and decreases to approximately 1 % at 100 Td.

Electron attachment is not observed for the species in Figure 4, but it may significantly contribute to the plasma dynamics with gas constituents of high electron affinities, such as O₂, O₃ or OH, thus is found among the basic mechanisms in discharges as sketched in Figure 3(d). The attachment occurs as a resonant process, predominantly at thermal electron energies up to approximately 10 eV and it leads to a sudden mass increase of the negative charge by at least three orders of magnitude. In other words, once captured, this negative charge immediately swaps its swift mobility of a low mass electron for the mobility of a species that eventually has to struggle its way to the anode with a longer dwell time inside the gap. This deceleration of negatively charged species significantly changes any discharge and plasma dynamics in the way that (i) the overall ionization rate per avalanche, and thus α , decreases and (ii) new regions of dense negative space charge may form, which essentially alternate the electrical field conditions.

2.1.1.6 Paschen Law

The *Paschen Law* is a well-established concept to illustrate whether the conditions with regard to gas pressure, electrode distance and applied voltage are sufficient for a *self-sustained* gas discharge. Its derivation is rather simple. Let us recall from section 2.1.1.2

that the breakdown threshold requires at least *one* further electron, on the average, to be liberated from the cathode by any sufficiently energy carrying species that was generated in *one* previous avalanche. Expressed in equations, we just need to equal equation (6) to unity, replace the coefficient α with Townsends equation (5) and finally rearrange for the voltage U , which now represents the breakdown voltage U_B . In this way we find the expression

$$U_B = \frac{B \cdot pd}{\ln(A \cdot pd) - \ln\left[\ln\left(1 + \frac{1}{\gamma}\right)\right]} \quad (8)$$

Most interesting is the correlation between the pressure p and the electrode distance d . Keeping the product of these two quantities constant will also keep the breakdown voltage constant. In other words, doubling the distance and at the same time reducing the pressure to one half will not change the breakdown characteristics. This inverse scaling of p and d reflects the fact that the potential difference for the electrons per mean free path remains constant in this case. All discharge phenomena in a gas are based on exactly this energy uptake from the field of an electron between two collisions. Consequently, also the total number of ionization and excitation events caused by an electron on its way from the cathode to the anode will remain the same with constant pd value. In his paper from 1889 [42], Paschen was the first who experimentally revealed this dependency and later, in 1910, Townsend provided the necessary theory [36] for deriving the semi-empirical relation shown in equation (8). This law holds true for an impressive large range of pd values in an uniform electric field. Deviations were found, e.g., in space charge dominating discharges, such as streamers [25] and in the field of miniaturizing discharges down to the microscale [43]. Still today it is of fundamental interest to eliminate the empirical part and derive expressions for A , B and γ based on first principles [38].

A typical plot of U_B as a function of pd is exemplarily shown for air in Figure 5. Note the double logarithmic scale. The values for A , B and γ are taken from [29] with $A = 1.13 \text{ mbar}^{-1} \cdot \text{mm}^{-1}$, $B = 27.38 \text{ V} \cdot \text{mbar}^{-1} \cdot \text{mm}^{-1}$ and $\gamma = 0.01$. Essentially, all gases show a similar shape of Paschen curve starting with a steep decrease down to a characteristic minimum and followed by a nearly linear trend over a large range of pd values to the right. At this point, let us recall the reduced field strength as defined in equation (3) and compare it to the Paschen curve (blue line). We immediately see that the slope $\frac{U_B}{pd}$ in Figure 5 simply represents the minimum reduced field strength E_r that is necessary for the breakdown to occur. In other words, it reflects the required mean potential energy for the electrons between two collisions, in order for the breakdown to occur at a defined pd condition. The functional relationship between E_r and pd for air is drawn by the black curve in Figure 5 with the respective scale on the right axis. Air shows a minimum in the Paschen curve of 305 V at 11 mbar·mm, which corresponds to a reduced field strength of

67 Td. Following the curve to the right branch we find the collision dominated regime where the total number of gas molecules between the two electrodes continuously increases. Roughly, one electron experiences about 150 collisions when traversing the discharge gap at the minimum of the Paschen curve and around 15 000 collisions at the largest pd of approximately 10 000 mbar·mm with a U_B of 45 000 V and a reduced field strength of 8 Td.

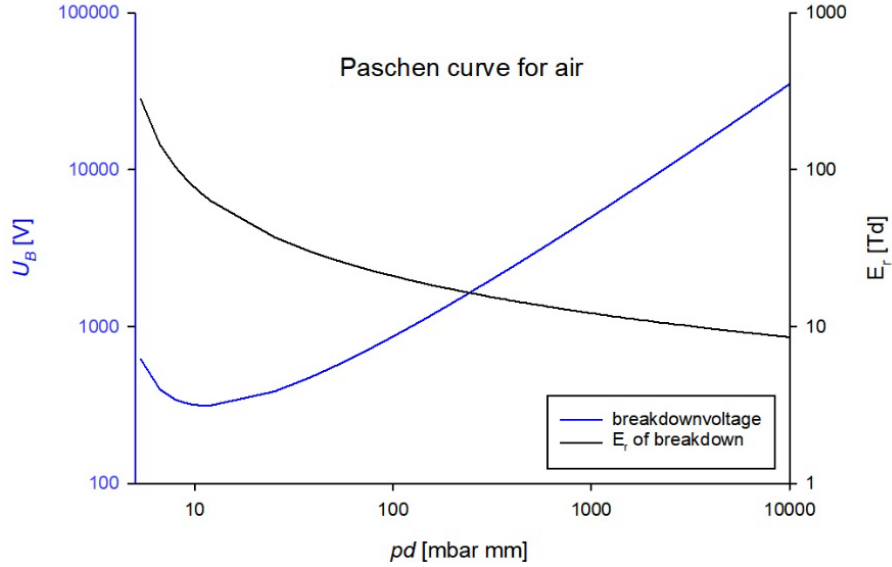


Figure 5: The blue line shows the Paschen curve for air according to equation (8) with values for A , B and γ taken from [44]. The black line represents the respective reduced field strength at the point of breakdown.

Consequently, on the right branch we find a small decrease of the required potential energy gradient between two collision by nearly a factor of eight. In equation (8) this trend is expressed by the logarithmic pd dependency of U_B in the denominator, which causes the linear pd trend of the nominator to slightly fall off to the right. Beyond those 15 000 collisions the number of ionization events leads to significant space charge effects and the breakdown is not simply explained by the mechanism of avalanche multiplication anymore. At the left-branch side of the Paschen minimum the total number of gas particles in the gap decreases and approaches the other extreme at which no atoms/molecules are left to collide with the traversing electrons. At this point the Townsend avalanche simply does not exist anymore and effects like field emission come into play [43, 45].

Despite its limitations, it is quite remarkable that the outlined concept of the breakdown based on the multiplication of Townsend avalanches applies over virtually four orders of magnitude of pd values. The Paschen curves provide a valuable tool for a multitude of areas where discharges may or may not be desirable, e.g., for the design of gaseous insulators or nuclear fusion reactors [46].

2.1.2 Space Charge and the Beginning of a Glow Discharge

Referring to Figure 2(b), we see that once the multiplication factor of the avalanches exceeds unity, not only does the discharge become self-sustained, but also the current swiftly increases by nearly six orders of magnitude without any change of the applied voltage. However, at some point in the micro to milli ampere region the number of slow-moving ions, which were left behind from the rushing electrons, becomes so large that space charge starts to affect the avalanche process. Dense positive ion clouds travel through the gap alike “gaseous” electrodes and thus significantly alter the electrical field. Instead of a constant electrical field strength, such as in the homogeneous field of the Townsend regime, zones of different field strength form across the gap. This causes electrons to pick up location dependent energy and a complex interrelation between the motion of the electrons through the gap and these positive ion clouds develops. Eventually, the *Townsend Discharge* turns into a glow discharge with its characteristic, different zones of alternating luminosity and dark regions, each an expression of the local variation of the respective electron energies [47]. In particular close to the negative electrode a positive cloud forms, which is responsible for the characteristic cathode fall. The high electrical field strength established between this proximate “gaseous” anode and the solid cathode essentially sustains the discharge by liberating electrons through ion bombardment and photon impact [29], followed by multiplication through avalanches. Consequently, less voltage is required across the solid electrodes from the external power supply to support the discharge and a voltage drop in the transition region from Townsend to glow discharge is observed (cf. Figure 2(b)). Once the discharge is in the glow mode, the current can be increased by several orders of magnitude without any change in the applied voltage. This is a consequence of the constant current density. With increasing current, the cathode area from which electrons are liberated equally increases and the limit in this discharge region is essentially determined by the dimension of the electrode. This phenomenon is visually reflected by the growth of the glow around the cathode [29]. When the entire surface is covered, a further increase of the current requires a higher electron flux density from the cathode. This involves higher voltages from the external power supply, as depicted by the steep incline of the curve in Figure 2(b) to the right.

2.1.3 Transition to Arc Discharge

To increase the electron current density beyond the glow discharge, a more intense ion bombardment on the cathode is required (cf. voltage incline to the right of the glow discharge in Figure 2(b)). However, each hit is accompanied by a certain amount of heat transferred to the electrode and the limitation of dissipating this energy causes the cathode to become hot. This changes the mechanism by which electrons are liberated for

sustaining the discharge. Instead of the required electron multiplication in the cathode fall in case of the glow discharge, thermionic processes start providing even higher currents, which are only limited by the power supply or the resistance of the external circuit. As depicted in Figure 2(b), the transition to this new mode, called arc discharge, goes along with a drastic decline to merely a couple of volts that are needed to sustain such large currents between the two electrodes [29]. The gas gap has finally become a reasonable conductor.

2.1.4 The Load Line

In practice it is quite advantageous to estimate the type of discharge that spontaneously develops for a given combination of power supply and gap condition (pressure, gas type, electrode distance, electrode size). In this regard, the load line, as depicted in Figure 2(b), has proven to be useful [29]. It is a straight line in U and i space, connecting the two extrema of maximum and zero voltage U at the electrodes. Equation (9) shows the linear relation for the load line, simply rearranged for some parameters for a better overview.

$$EMF = U + i \cdot \Omega \quad \Rightarrow \quad U = -i \cdot \Omega + EMF \quad \Rightarrow \quad i = \frac{EMF - U}{\Omega} \quad (9)$$

In the first case, the resistance Ω in the power supply and external circuit is infinitely large, the current i converges to zero and the voltage U at the electrodes simply equals the electromotive force EMF of the power supply. In the latter case, U is zero and the limiting current that can be provided by the power supply and the external circuit equals the ratio of EMF/Ω (cf. Figure 2(b)). The farthest crossing point of the load line with the characteristic $U - i$ discharge curve determines the discharge type and the actual U, i values that establish under the given conditions between the electrodes, as exemplarily shown for the glow mode in Figure 2(b). Note that the key parameter for the developed mode is the current, since it determines the degree of ionization and the extent of space charge. Consequently, the current that can be supplied by the power supply and the external circuit distinguishes between a Townsend, glow or arc discharge and anything in between. For a given gap condition, basically two variables are available to switch between different discharge types, the resistance and the EMF . Let us consider the load line in Figure 2(b). In order to change from a glow to a *Townsend Discharge* with the same gap condition and the same EMF , the load line simply requires a steeper decrease through increasing the circuit resistance, in practice with an additional ohmic resistor between the power supply and the gap. On the other hand, lowering Ω , e.g., with more conductive wires or a new power supply with a lower internal resistance, flattens the decline and a transition to an arc discharge occurs. The second option for this transition is to increase the EMF at constant Ω , which simply shifts the load line parallel to the right in the $U - i$ diagram.

It is emphasized that these considerations are more of qualitative and only approximate quantitative value, since the U, i curves are very specific and are simply not always at hand for every gap condition. Nevertheless, this load line concept allows for rather practical guidance how to establish or prevent a certain discharge mode based on the applied electrical circuit.

2.1.5 Miniature Spark Discharge

The reader may have noticed the missing spark regime in the general outline of the current-voltage diagram of Figure 2(b). All discussed discharge types along that curve are rather constant over time, as long as the power supply is switched on and the load line is clearly defined. In contrast, the spark shows a transient character that automatically extinguishes after a short period of time. Typically, this behavior is caused by a limited load of excess electrons on the cathode side, which generates the voltage drop across the gap. Once the discharge starts, those electrons are depleted from the cathode without being reproduced by an external supply. This causes a gradual decrease of the electrical field and at a certain point the discharge finally extinguishes. The second characteristic of sparks is the rapidness of electron depletion, along with low gap and circuit resistance and consequently high current densities. In terms of the load line in Figure 2(b) the EMF/Ω ratio for spark discharges is quite high, resulting in current limits in the arc region. In fact, a swift transition of a spark into an arc discharge with all its features as described in 2.1.3 is exactly one observes, when increasing the electron load on the cathode side. Consequently, as pointed out by Raizer [30], the spark discharge can be regarded as a transient arc, since it is also characterized by a vanishing gap resistance, however, only for a short period of time. In case of a pulsed high voltage charger with a capacitor assembly, this arc transition is easily realized by either increasing the charging frequency and/or the charging length.

3 Spectroscopy and Current-Voltage Characteristics

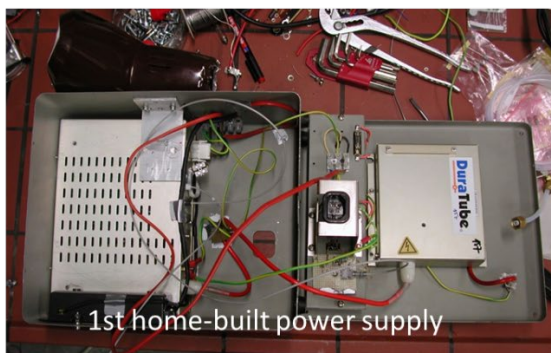
3.1 Experimental Setups

3.1.1 Power Supply

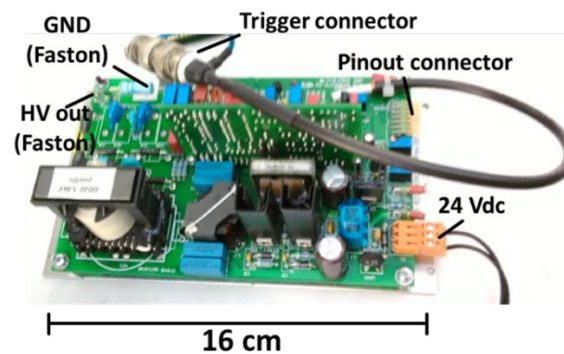
The key to successfully operate the miniature spark discharge lamp in Figure 1 was the right combination of electrode assembly, gas- and power supply. For the latter several attempts were made based on high voltage DC/DC converters, neon-sign transformers and from old computer monitors recycled flyback transformers. However, they all failed in particular due to the uncontrollable repetition rates, which were merely determined by the self-oscillation up to 20 kHz. In many cases the high-voltage transformation

processes started to overlap with the single spark events and fed additional electrons to the discharge. As discussed in chapter 2.1.5, when the amount of electrons per sparking event is not strictly limited on the cathode side, the discharge turns from its transient character into a continuous plasma with the limiting currents of the load line located in the arc region (cf. chapter 2.1.4). Consequently, several lamp setups severely suffered from changing into arc discharges with the characteristically overheated electrodes (cf. chapter 2.1.3). The additionally limited heat conductivity eventually destroyed the entire lamp cavities.

The first power supply meeting the requirements for a sustained lamp operation was built from a switch-mode power supply (HPE CC400, Hartlauer Präzisions Elektronik GmbH, Grassau, Germany) recycled from an exciplex laser (cf. Figure 6(a))[48]. In such gas laser systems the power supplies repeatedly charge a series of capacitors to a certain breakdown voltage and the subsequent electrical discharge generates the exciplex species responsible for the laser radiation. In combination with an opto-coupler and a digital delay generator this power supply provided 14 kV and 60 mA average current with an adjustable repetition rate between 1 and 2000 Hz. For some lamp configurations, however, the delivered electron load on the cathode exceeded the sparking limit and an arc transition was observed again. This issue was resolved by simply adding an ordinary 60 W light bulb as resistor in series with the mains power supply of the high voltage generator. In case of an arc transition the increased current through the circuit briefly heated up the filament of the bulb in a short flash. As discussed in detail in chapter 2.1.4 this temporarily increased resistance Ω of the external circuit caused a steeper load line and consequently a transition to a discharge mode with less current. The light bulb thus served as a self-regulating resistor in this entire circuit to constantly restore the sparking conditions and prevent the electrodes from overheating.



(a)



(b)

Figure 6: Spark discharge power supplies. (a) The first functioning home-built power supply recycled from an exciplex laser system [48] and (b) the final custom designed power supply in cooperation with Hartlauer Präzisions Elektronik GmbH [49].

However, designed for driving larger discharges, the HPE CC400 oversupplied the miniature spark lamp. With certain sensitive peripheral equipment severe electromagnetic interference was observed. Accordingly, in cooperation with Hartlauer Präzisions Elektronik GmbH, a smaller version of a switch-mode power supply was custom designed and tailored to the specific needs of the miniature spark lamp. As shown in Figure 6(b) [49, 50] a small-sized circuit board (DD2010 C-Lader) was constructed with a 24 V/ 30 W feed, an external trigger connector, an HV output and a 14-pin connector to, e.g., monitor and remotely adjust the high voltage and current output. This device provides voltages up to +1 500 V on two capacitors of 1 nF each, charging currents up to 15 mA and a charging repetition rate of up to 1 500 Hz. The circuit board was built into a housing together with a 24 V DC supply (DPP 50-25, TDK-Lambda Germany GmbH, Aachen, Germany), a cooling fan, and a home-built trigger board based on a NE556N timer.

Figure 7 [24] depicts the electronic characteristics of the final power supply in combination with the spark lamp setup shown in Figure 1. In Figure 7(a) the temporal correlation of the current and voltage evolution at a frequency of 1 500 Hz is illustrated by three consecutive breakdowns. The distance between each breakdown precisely matches the 0.66 ms and the breakdown current and voltage are sufficiently stable within 10 %. A single breakdown, as well as the corresponding trigger pulse are presented in Figure 7(b). The optimum trigger width was determined as 0.18 ms. The response time for the charging process is 0.05 ms and the breakdown occurs after 0.13 ms, during which the trigger is still high. Consequently, the switch-mode supply continuously charges the capacitors during the breakdown event, however, with a rate insufficient to sustain the plasma and to cause an arc transition. The discharge finally extinguishes, while the trigger is still high for 0.03 ms. With an additional response time of 0.05 ms the switch-mode supply eventually recharges the capacitors to a ground level of approximately 200 V before the next trigger event.

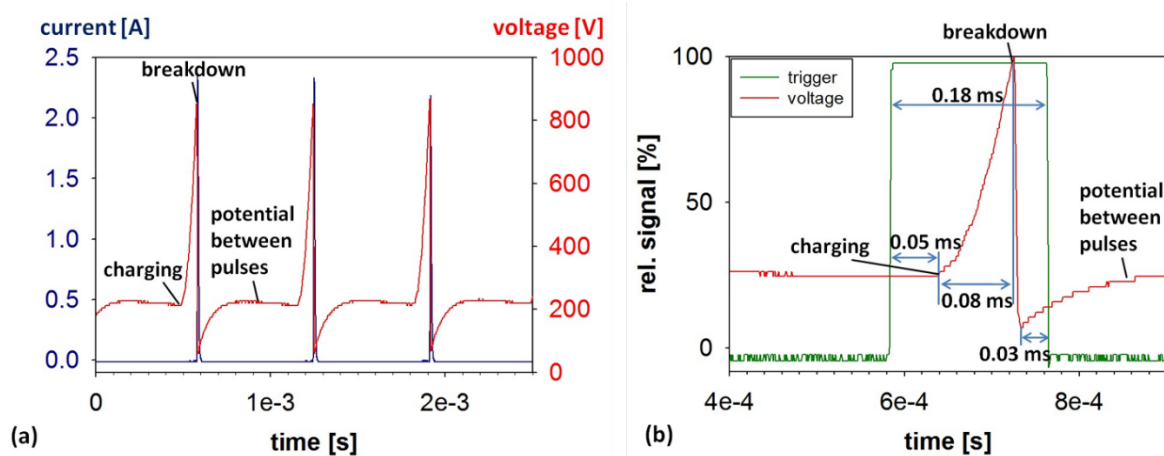


Figure 7 [24]: Electronic characteristics of the final spark plasma power supply DD2010 C-Lader. Temporal evolution of the current and voltage of (a) consecutive spark events and (b) a single spark event as a close-up.

3.1.2 Electrode Assembly

Wavelength resolved emission data in the near infrared, visible and ultraviolet region down to approximately 200 nm are readily available with optical fiber spectrometers. Even in less accessible plasma configurations, such as the original capillary setup shown in Figure 1, the fiber is easily adjusted onto the window to pick up light. In stark contrast, emission spectroscopy in the vacuum-ultraviolet region requires a dedicated setup with precise alignment of the plasma immediately in front of the entrance slit of the spectrometer. Consequently, as described in the DFG grant [2], to cover the proposed broad spectroscopic range in combination with the corresponding time resolved current-voltage characteristics, the spark assembly had to be redesigned and adapted to the specific technical needs of the VUV-spectrometer. Along this line, Dr. Kai Kroll qualitatively described the impact of different electrode shapes on the spark behavior in his bachelor thesis [9]. Figure 8(a) depicts the four different types under investigation. The material (stainless steel), distances and also the discharge gas flow conditions remained comparable. Kroll observed temporally as well as spatially very unstable discharges for the configurations #2, #3 and #4. Variation of the pressure as well as the gas flow did not change the unfavorable spark characteristics in terms of operating the setup as a high to medium pressure, small spot-sized and brilliant VUV lamp.

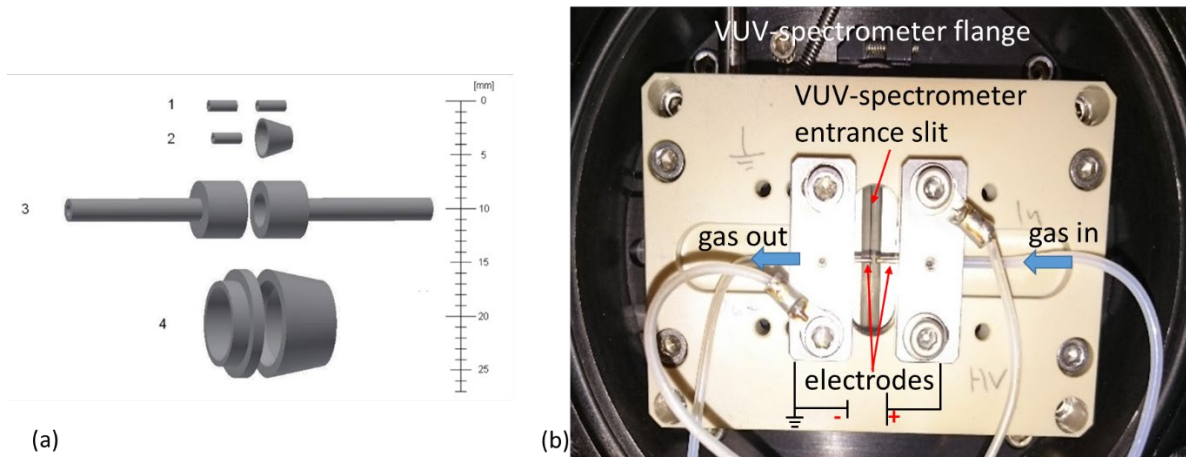


Figure 8 [9]: (a) Spark electrode configurations under investigation and (b) final electrode setup in front of the VUV-spectrometer.

Only the original electrode configuration #1 from the capillary design showed this unique spark behavior. Accordingly, medical stainless steel cannulas of 1 mm outer diameter and of 0.25 mm wall thickness were adapted to the VUV-spectrometer entrance as electrodes (cf. Figure 8(b)). The needle tips were carefully grinded to a blunted end and visually inspected under a microscope for their cleanliness. On a PEEK holder, mounted to the spectrometer, two movable stainless-steel slides clamping the electrodes allowed for the precise horizontal and vertical alignment of the discharge gap and its length. High voltage was supplied through wires connected to the slides and on the other end connected to

BNC feedthroughs in the spectrometer flange. The discharge gas was supplied through 1.6 mm Teflon® tubing tightly fitting the electrodes and connected to the corresponding gas feedthroughs on the spectrometer flange. If not otherwise stated, the electrode distance was adjusted to 0.5 mm, measured with a caliper.

3.1.3 Gas Supply and Vacuum System

As depicted in Figure 9, the vacuum system, gas supplies and all diagnostic tools were centered around a modified VUV-spectrometer Arc Model VM-502 (Acton Research Corporation, Acton, MA, USA). High vacuum down to $2 \cdot 10^{-6}$ mbar was generated with a turbomolecular/drag pump combination. A gate valve between the turbo pump and the spectrometer allowed for rapid gas filling with a VUV transparent background gas up to the required operating pressure. Spectroscopic measurements demonstrated that this procedure efficiently reduced contamination through leakages. A needle valve-controlled bypass between fore pump and the gas outlet regulated the pumping speed through the cathode. The key concept for a windowless and completely transparent (>40 nm) light path between the plasma emission and the VUV dispersive unit required particular precautions for the cleanliness of the grating chamber. Therefore, a flow of the background gas with approximately 50 sccm was introduced at a backside port of the spectrometer, continuously flushing the chamber and exiting through the entrance slit (cf. Figure 9) during plasma operation. This efficiently prevented reactive species and feasible sputtered aerosols from contaminating the dispersive unit. Three flow controllers were used to provide discharge gas mixtures of two components and introduce them through the anode. Special care was taken for short and small diameter tubing to allow for rapid changes of the discharge gas settings without any carryover.

The entire system was designed to provide isobaric discharge conditions between 400 mbar and 1700 mbar, with discharge gas flows up to 350 sccm of admixtures with two components in the ppbV up to percent regime. If not stated otherwise, all used gases were purchased with a stated purity of 99.999 %. The major component was additionally purified with a VICI gas purifier (HP2, Valco Instruments Co. Inc. International, Schenkon, Switzerland) to impurity levels below 10 ppbV, as stated by the manufacturer.

3.1.4 Spectroscopic Setup

3.1.4.1 VUV Spectrometer

A scanning VUV-spectrometer Arc Model VM-502 (Acton Research Corporation, Acton, MA, USA) from the 1980s was completely refurbished and used in V-mode for the wavelength range between 40 and 200 nm (cf. Figure 9). It was equipped with a rotatable

Al/MgF₂ coated holographic grating with 1 200 lines per mm and a focal length of 20 cm, providing a wavelength resolution of approximately 1 nm (fwhm). An external motor with four different, constant speed levels allowed for precise scanning conditions and replaced the original, damaged gear box.

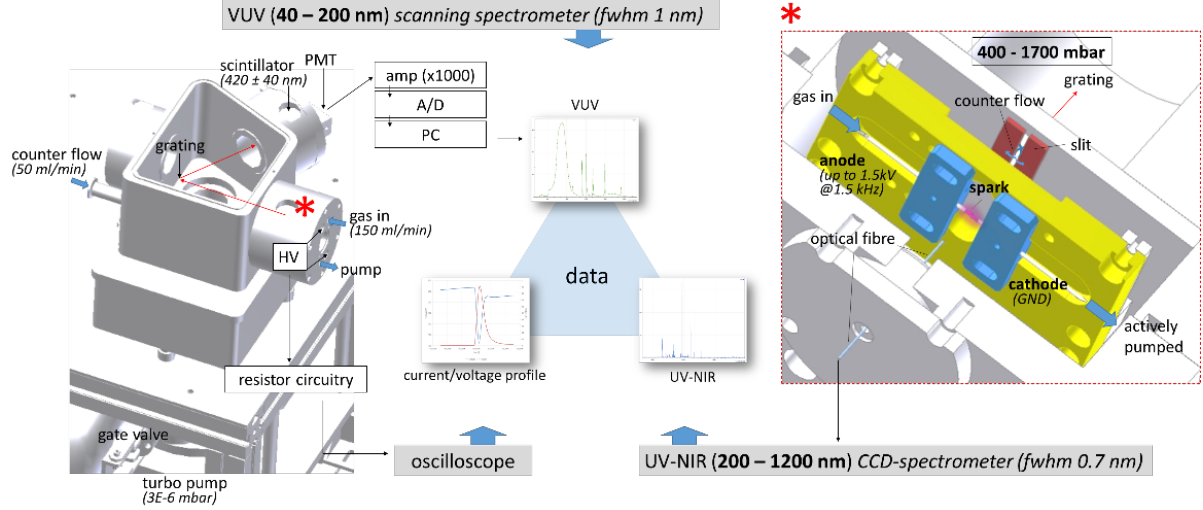


Figure 9 [18]: Diagnostic setup for spark discharge investigations, including VUV and UV-VIS-NIR spectroscopy and time resolved current and voltage measurements.

The detection unit had to be completely redesigned as well. In particular the intended measurements below 100 nm at elevated pressures required a new concept. Typically, the VUV source, the grating chamber and the photomultiplier tube (PMT) are separated by window materials such as MgF₂ or LiF, with a lower wavelength cut-off at 110 nm and 105 nm, respectively [51, 52]. To date, no transparent material for the range between 105 nm and approximately 10 nm is known. Only very thin aluminum foils show a small transparency region between 84 nm and 17 nm and are completely transparent for wavelength below 10 nm [53]. The PMT employed is usually a solar-blind type, with tailored sensitivity in the VUV spectral range, however, limited to the mentioned 105 nm at least. Operating a PMT without a window at elevated pressure is not possible due to the electron avalanche mechanism that multiplies the incident photons to a measurable current. The required high electrical field strength between the discrete dynodes would cause a plasma in any gas at elevated pressure and finally damage the PMT. Consequently, to extend the scan range down to 40 nm, basically two measures were needed: (i) A windowless integration of the plasma source in front of the spectrometer entrance with all the necessary precautions, as described in section 3.1.2 and (ii) a suitable conversion of the diffracted high-energy photons to wavelengths, which can pass the window of a common PMT at the spectrometer exit. Therefore, an essential part of the VUV measurements in all projects reported here was the right coating of a suitable scintillator on a window substrate, placed inside the spectrometer between the grating and the PMT. This coating should provide high and constant conversion efficiencies between 40 nm and

200 nm into a wavelength matching the sensitivity maximum of the PMT. Furthermore, the coating thickness was to be optimized to efficiently capture the incident high energy-photons and, on the other hand, to efficiently transmit the fluorescence light through the window to the PMT.

Dr. Michael Dlugosch was one of the first bachelor students in the field of *Plasma Research* during the period covered in this work and he successfully addressed the scintillator task [8, 54]. His work was based on the publications by Knapp, Kristianpoller et al., Kumar et al. and Al-Kuhaili [55-58], who used either spin-coated or solvent-sprayed films of sodium salicylate as a scintillator. According to the literature, this salt meets all the requirements stated earlier. In particular the outstanding and nearly constant conversion efficiency between 40 and 350 nm into a broad and convenient fluorescence signal peaking at 420 nm makes that compound a suitable scintillator. Michael Dlugosch built a coating setup based on a regular piezo nebulizer as shown in Figure 10(a), which was capable of producing homogenous coatings with reproducible layer thickness. Through a regulated inlet the liquid level of a 0.1 M sodium salicylate solution dissolved in distilled water was kept constant above the nebulizer to maintain a steady fog density. An air flow of 1 slm to 3 slm continuously transported the fog through an outlet tubing onto a heated glass substrate. To obtain a well-defined coated spot, a simple round mask additionally restricted the area on the substrate. Mr. Dlugosch showed that this setup provided reproducible and precisely adjustable layers through a simple linear dependency between coating time and the resulting thickness (cf. Figure 10(c)). As shown in Figure 10(d), he also found an optimum at approximately $30 \text{ mg}\cdot\text{cm}^{-2}$ for the coating thickness with respect to the transmitted fluorescence intensity. In accordance with the literature, the spectrum in Figure 10(b) nicely exhibits the broad fluorescence peak of the coatings at around 420 nm upon excitation with a regular krypton low pressure discharge lamp emitting at 116 nm and 123 nm (cf. section 3.1 in chapter III HELICAL RESONATOR PLASMA). This procedure provided a convenient, fast and low-cost way for frequent replacement of the aged coatings on the exit window.

In most VUV-spectroscopic measurements, a R928 or a R955 PMT (Hamamatsu Photonics, K.K., Hamamatsu City, Japan) was used to pick up the fluorescent light of the sodium-salicylate coated exit window. With a maximum spectral response at 400 nm, both PMTs match the fluorescent maximum quite well (cf. Figure 10(b)).

The PMT signal was further amplified with a home-built operational-amplifier circuit providing a gain factor of up to three orders of magnitude. With an A/D converter (R232-ADC16/24, taskit GmbH, Berlin) the analog signal was digitized and further processed in a comprehensive custom software VUVRecSpec 1.15 [59]. The A/D converter also allowed for digital output, which was used to control the external motor via a 240 V relay in order

to integrate the physical scan start and stop procedure into the software and synchronize with data recording. Spectra are directly visualized in a chart and saved in a x,y-textfile format including the prevailing instrument settings. Within the same program, files can be loaded, compared and post-processed with standard chart tools for full analysis. Therefore, VUVRecSpec 1.15 provides a comprehensive and automated control, data recording and data analysis software and turned the old Arc Model VM-502 into a fully software controlled VUV-spectrometer.

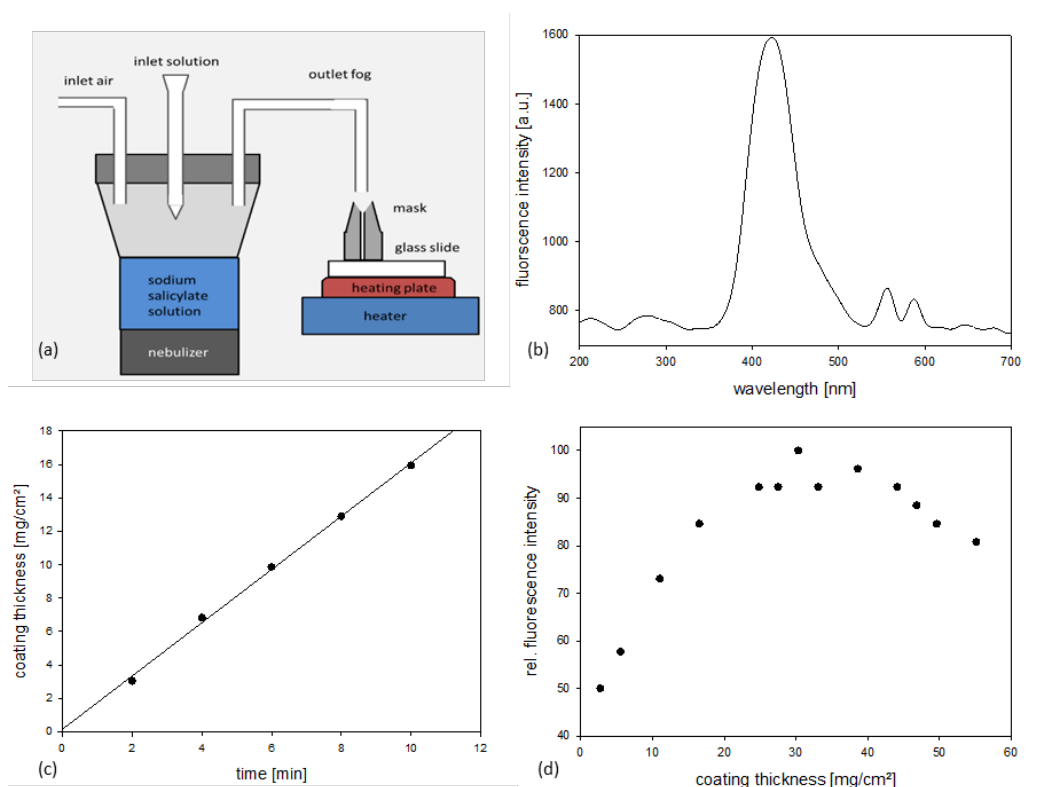


Figure 10 [8]: (a) Schematic of the scintillator coating setup. (b) Wavelength resolved spectrum of the fluorescent light upon irradiation of the scintillator coating with incident VUV-light at 116 nm and 123 nm from a low-pressure krypton discharge lamp. (c) Dependence between coating time and coating thickness. (d) Dependence of measured fluorescence intensity on coating thickness.

3.1.4.2 UV-VIS-NIR Spectrometer

The wavelength range between 200 nm and 1100 nm was covered by a fiber optic AvaSpec-3648 spectrometer (Avantes BV, Eerbeek, The Netherlands) with a resolution of 0.7 nm (fwhm). An original optical fiber was cut with special care taken for producing a smooth and even surface. The cut side was fed through the VUV spectrometer flange, aligned and placed approximately 5 mm in front of the spark region (cf. Figure 9 inset). A standard Vespel® ferrule as used for gas chromatography (GC) setups ensured a vacuum tight sealing. The AvaSpec-3648 features 16-bit digital resolution data acquisition and shows excellent linearity with integration time, as depicted in Figure 11 for the weak 318.7 nm line of the $(1s4p)^3P_2 \rightarrow (1s2s)^3S_1$ transition in a helium spark discharge at

1 200 mbar. This allows for different intense wavelength regions to be subsequently recorded with altered integration times and normalized on these. The signal-to-noise ratio (S/N) shows an asymptotic slope with increasing integration time approaching a maximum enhanced S/N of approximately four.

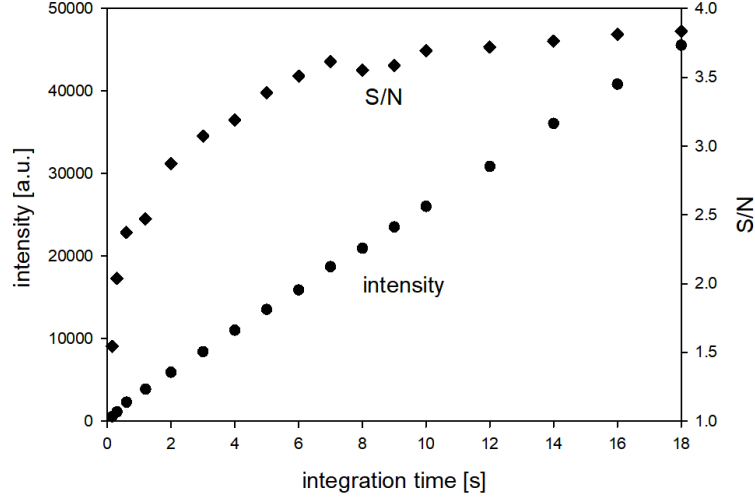


Figure 11: Recorded intensity and signal-to-noise (S/N) in dependence of the integration time for the weak 318.7 nm line of the $(1s4p) \ ^3P_2 \rightarrow (1s2s) \ ^3S_1$ transition in a helium spark discharge at 1 200 mbar.

3.1.5 Current/Voltage and Time Resolved Light Measurement Setup

Figure 12 shows a picture and a diagram of the electrical circuit used to monitor the time resolved voltage U between the anode and the cathode, and the time evolution of the current I flowing from the cathode to ground. As depicted, a 1:1 000 voltage divider with a 100 M Ω and 100 k Ω in series to ground was used to monitor U . To quantitatively resolve the current I , the voltage-drop across a high-precision 1.00 Ω resistor between the cathode and ground was used. The entire circuit including a short BNC connector revealed a measured deviation of $\pm 0.1 \ \Omega$, which results in a relative error of $\pm 10 \%$ for all the current measurements. Design and assembling was done by Sebastian Klopotoski, a PhD student funded via the referenced DFG grant [2].

For the time and also wavelength resolved light measurements in the VUV the relatively fast response of the photomultiplier tubes (R928 or R955) were used (cf. 3.1.4.1). Both PMTs show an anode pulse rise time and an electron transit time of 2.2 ns and 22 ns, respectively. A fast photodiode (DET025AFC/M, Thorlabs, Inc., Dachau, Germany) with a response time of 122 ps was used to record the temporal evolution in the VIS-NIR as the total emission between 400-1 100 nm. The diode provided a fiber connector for swift adaption to the installed spectrometer fiber (cf. Figure 9, inset)

For all time resolved measurements either a LeCroy LT344 or an RTE 1054 from Rohde & Schwarz GmbH & Co. KG (Munich, Germany) were used as oscilloscopes, the latter specifically purchased from the referenced DFG grant for this project.

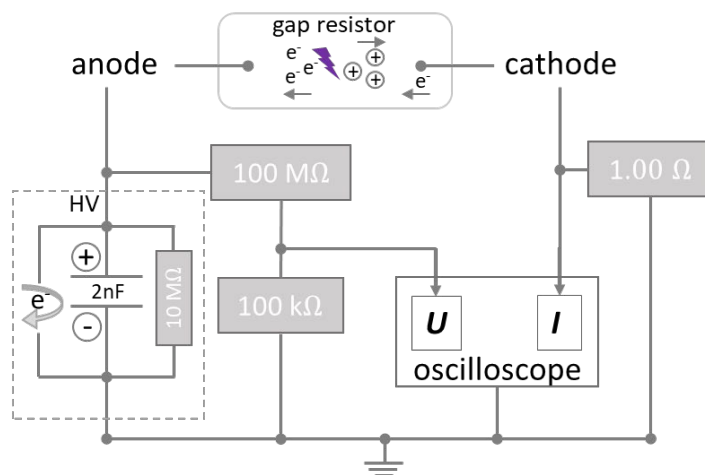
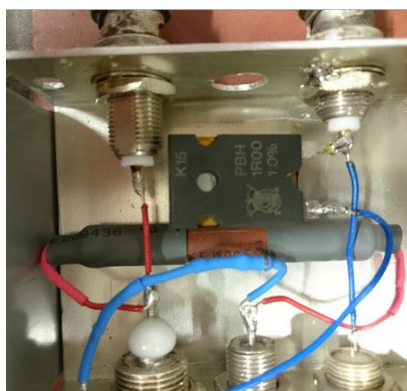


Figure 12: picture and a diagram of the electrical circuit used to monitor the time resolved voltage U between anode and cathode, and the time evolution of the current I flowing from the cathode to ground.

3.2 Spectroscopy

3.2.1 Comparison with Commercial VUV Lamps

As briefly mentioned in chapter 2, the miniature spark discharge was initially designed as a spatially confined and bright VUV photon source to efficiently ionize gas stream components flowing inside a capillary conduct of the gas inlet stage of an API mass spectrometer. It was successfully demonstrated that the spark position along the capillary allowed for wide kinetic control of the ion molecule chemistry [21]. However, the performance with regard to VUV emission as compared to conventional low-pressure RF driven VUV lamps (krypton filling) used in APPI-MS remained unclear. This question was further investigated as part of the DFG grant miniature spark discharge lamps [2].

The illuminated spot size is one major difference between conventional APPI lamps and the miniature spark discharge, with diameters of 8 mm (cf. section 3.1 in chapter III HELICAL RESONATOR PLASMA) and below 1 mm, respectively. However, preliminary results suggested that despite its smaller size the ionization efficiency of the miniature spark is comparable and even outperforming the conventional lamp under certain circumstances. The second significant difference is the window required for the low-pressure plasma used in conventional APPI lamps (cf. section 2 in chapter III HELICAL RESONATOR PLASMA). As already discussed in detail in the course of the VUV-spectrometer modification (cf. chapter 3.1.4.1), a LiF window provides the lowest possible cut-off at 105 nm, which still severely restricts the effectively usable VUV light generally available from most plasmas. However, it is mentioned that in general manufacturers equip the lamp housing even with MgF_2 (cut-off at 110 nm) instead of LiF windows due to its higher durability. The surface of LiF tends to turn yellowish over time (solarization) [60]. This imposes additional severe transmission limitations. In contrast,

the spark source can be operated in a broad pressure range without the need of a window sealed enclosure. Apparently, this offers more flexibility to use ionizing VUV photons even below this limiting cut-off. For these two reasons, it was of high interest to further investigate the capabilities of the mini spark discharge with regard to ionizing radiation in a broad wavelength range down to 50 nm and compare the output with a conventional VUV lamp. As soon as the spectroscopic setup was finished (cf. chapter 3.1.4.1), first results were shown at the annual conference of the American Society for Mass Spectrometry (ASMS) in 2012 [49]. Figure 13 depicts some of the results presented. For comparison, a typical APPI setup comprised of a PhotoMate® RF plasma driver from Syagen Technology Inc. (Tustin, CA, USA) equipped with a PKR 106 low-pressure krypton lamp from Heraeus Noblelight (GmbH, Hanau, Germany) was used. Note, the manufacturer also equipped this lamp with a MgF₂ window for stated reasons. The spark discharge as well as the APPI lamp were directly positioned in front of the entrance slit (width 0.25 mm). The recorded intensities thus resemble a rectangular section of $0.25 \cdot 8 \text{ mm}^2$ from the APPI lamp and the full spot size of approximately 1 mm in diameter of the spark lamp, respectively.

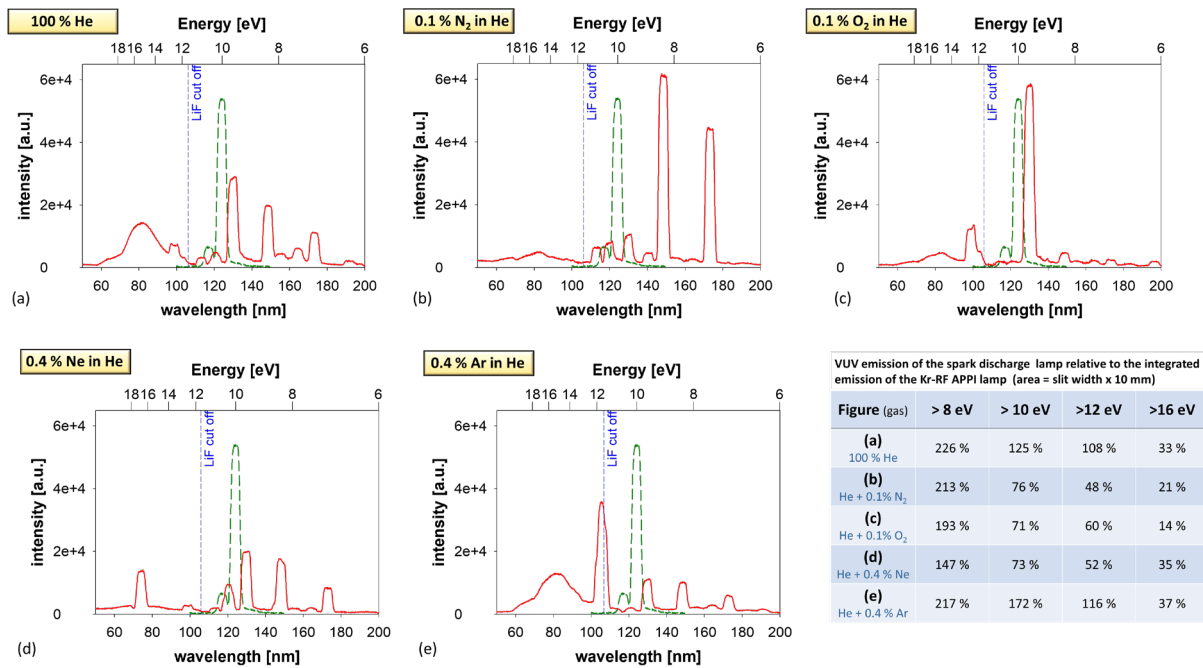


Figure 13 [49]: VUV spectra comparing a commercial APPI lamp and the helium spark discharge emission with different additives, (a) 100 % He, (b) 0.1 % N₂, (c) 0.1 % O₂, (d) 0.4 % Ne and (e) 0.4 % Ar. The table lists the total VUV output of all admixtures in four different energy regions relative to the APPI lamp.

The green dashed curve represents the spectrum of the low-pressure Kr-RF lamp with the line emission at 123.6 nm (10.0 eV) and 116.5 nm (10.6 eV). Both transitions initiate from a $4s^24p^55s$ electron configuration and terminate in the $4s^24p^6$ electronic ground state [61]. The involved terms are the $^1S_0$ for the ground state, the $^2[3/2]_1$ and the $^2[1/2]_1$ for the 10.0 eV and 10.6 eV electronically excited states, respectively. The observed intensity of the 10.6 eV line is approximately 12 % of the 10.0 eV emission, which clearly indicates

strong transmission discrimination of the lower wavelength caused by the MgF_2 window. Comparable plasma conditions without windows have shown intensity ratios of 3:4, which nicely matches our own spark measurement results with a helium/krypton mixture shown in chapter 3.2.2. To further demonstrate the adverse window impact, the blue dashed line marks the LiF threshold in each spectrum in Figure 13. Again, this being the lowest possible cut-off for a window, below which any plasma emission is completely absorbed. The spectra of the mini spark lamp are shown as straight, red lines. Different gases were used to show the flexibility in VUV emission and compare the total output. In each case helium was chosen as the main component since it has the largest gap between the ground and first electronically excited state of 19.8 eV ($^3S_1$) for the metastable state and 20.9 eV ($^3P_2$) for the first optically allowed state. N_2 , O_2 , Ne and Ar were added up to 0.4 %. The discharge pressure was maintained at 950 mbar.

As a first qualitative estimate the integrated VUV emissions of all spark spectra in Figure 13 seem comparable to the integrated emission of the APPI lamp despite the significantly smaller spot size. In the cases of 100 % helium and with O_2 , Ne and Ar addition, also significant radiation emission below the LiF cut-off was observed. The table shown in Figure 13 provides a more quantitative description with the total emitted radiation in certain energy ranges relative to the recorded range of the Kr-RF spectrum. Please note, the recorded intensities were not corrected by the wavelength dependent reflectivity of the spectrometer grating. Therefore, the results might even underestimate the intensity of the lower wavelength range. As mentioned previously (chapter 3.1.4.1), the scintillator conversion efficiency, however, is constant throughout the covered wavelength range. With “pure” helium, the mini spark lamp provides more than twice as much light (226 %) above 8 eV and 125 % above 10 eV, as compared to the total APPI output. Approximately as many photons as the Kr-RF lamp emits between 10 and 11 eV are emitted by the spark discharge above 12 eV and 33 % even above 16 eV. Consequently, this lamp is capable of emitting abundant high energy photons at atmospheric pressure, which can be applied without any restricting window material. Note that this “pure” helium spectrum shows strong signatures of impurities, which will be discussed in detail in the following chapter 3.2.2. Figure 13 also demonstrates the flexibility for swiftly adjusting the radiation energy. With the addition of 0.1 % nitrogen to the discharge gas the spectral intensity significantly shifts to higher wavelength, with strong emission centered around 140 to 180 nm ($\sim 7\text{-}9$ eV). However, approximately three quarters of the total output still remain above 10 eV as compared to the Kr-RF lamp. With the addition of 0.1 % oxygen the mini spark lamp obtains comparable photon fluxes within the emission range of the APPI lamp, just slightly shifted by 0.7 eV to lower photon energy. Due to a strong signature at around 100 nm, just below the LiF cut-off, the He/ O_2 mixture can still supply up to 60 % photon flux above 12 eV as compared to the total APPI

flux. The VUV performance of the helium/neon mixture was rather disappointing with regard to the total flux as well as to the energy range. The total emission significantly decreased as compared to the “pure” helium spectrum and the previous strong and broad emission at around 82 nm was replaced by a smaller and less intense peak at around 75 nm (16.5 eV). In stark contrast, the addition of 0.4 % argon seemed to retain the original 82 nm emission and add an additional strong emission right at the LiF cut-off at 105 nm (11.8 eV). Consequently, this mixture showed the strongest radiation with photon energies above 10 eV and even above 12 eV as compared to the other investigated gas compositions. In the following chapter 3.2.2. more detailed spectroscopic features will be discussed with respect to the involved electronic transitions and plasma dynamics causing the observed characteristic spectroscopic features.

In summary, the first VUV-experiments in 2012 have clearly demonstrated the capabilities of the mini spark as a photoionization source for use in applications such as mass spectrometry. In contrast to conventional low-pressure plasma lamps (e.g., Kr gas filling) with pure line emission and restricted transmission, the mini spark lamp allows adjustable photon energies between 7 and 17 eV in a large pressure range. The total VUV photon flux is comparable, the photon density even outperforms the conventional lamp by an order of magnitude. This renders the mini spark particularly interesting for applications, where high brilliance combined with high and flexible photon energies on a small spot size is required. The unique combination of high pressure and adjustable high photon energies also enables interesting fundamental investigations on novel photo ionization characteristics at atmospheric pressure, e.g., auto ionization vs. photo dissociation. Furthermore, compared to other atmospheric pressure discharges, only relatively minor hardware (power supply) and gas effort is required for operation.

3.2.2 Detailed Spectroscopic Investigation

In 2012, funded by the DFG grant [2], the PhD student Sebastian Klotowski continued the preliminary spectroscopic work as reported in chapter 3.2.1 in more detail. As pointed out for the results depicted in Figure 13(a), a strong signature of persistent impurities was apparent between 100 nm and 200 nm, despite the 100 % ultra-clean helium being used. All of the peaks can be assigned to emissions from oxygen, nitrogen and carbon. Several tedious attempts were needed to find out the optimal evacuation and filling procedure of the experimental setup. Even a sealed plastic sheet cover of the setup, evacuated and filled with helium was tested to minimize the spectroscopic noticeable impact of impurities. At the ASMS conference in 2014 [62], we finally presented experimental data on some of the purest VUV spectra (40–200 nm) of an atmospheric

pressure helium discharge, which are, to the best of our knowledge, available in the literature. Figure 14 shows some of the results reported (wavelength given in Å).

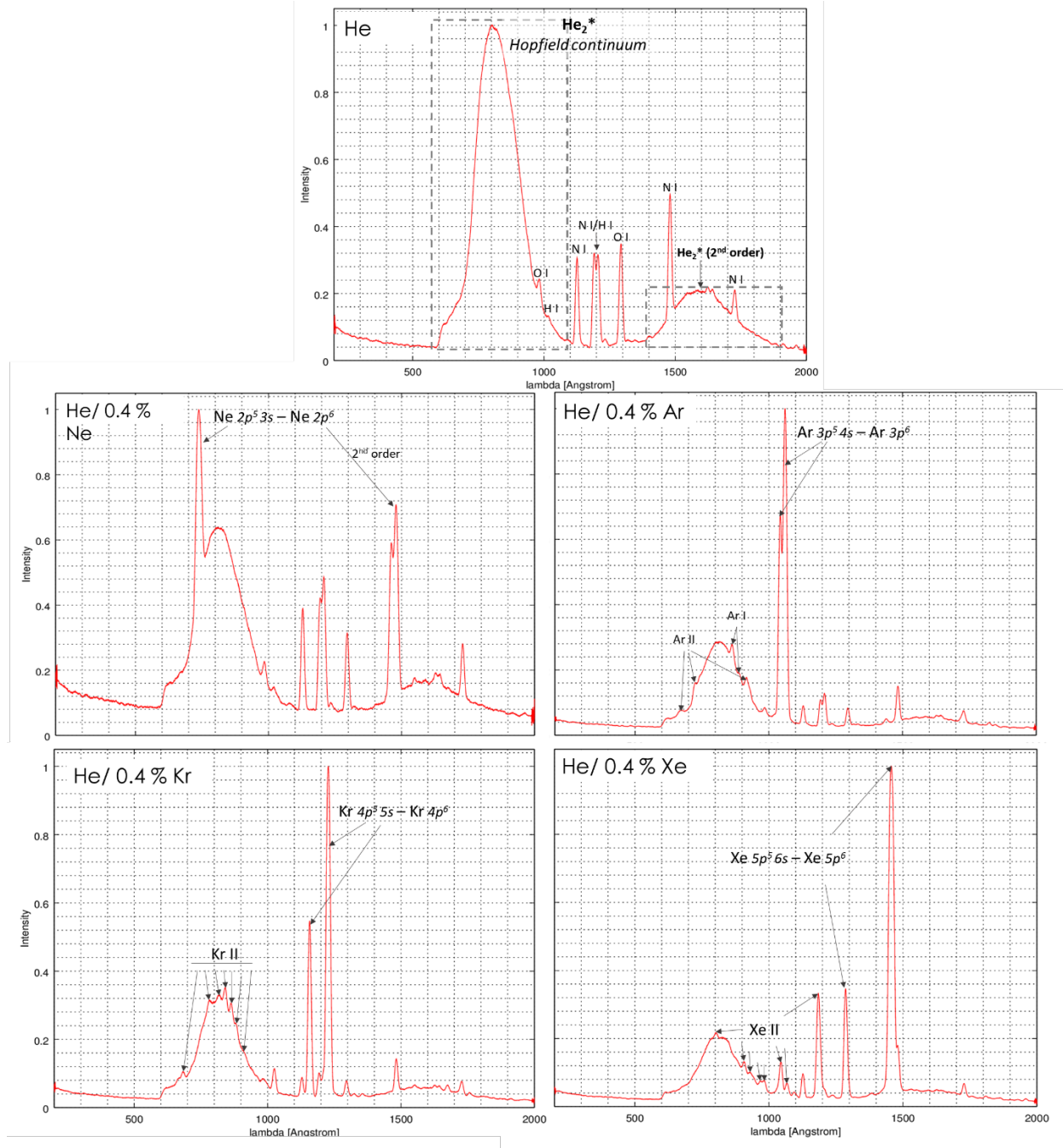


Figure 14 [62]: VUV spectra of the helium spark discharge with considerably improved background purity. Shown are spectra of 100 % He and mixtures containing 0.4 % each of Ne, Ar, Kr and Xe.

What is striking is the extreme intense and exceptionally broad helium emission between 60 nm and 100 nm with a maximum at approximately 82 nm. It is additionally seen in the second order of the angular dispersion of the grating, centered at around 164 nm with regard to the first order scale. In the pure helium discharge, only minor contributions of H(I), O(I) and N(I) were observed. The most prominent wavelength and the corresponding transitions are listed in Table 1 further below. This high purity allowed for

more profound investigations regarding the effects of the successive addition of minor gas components (e.g., neon, argon, krypton, xenon) to the helium discharge. Of particular interest was the plasma chemistry and the corresponding changes in the VUV region, which is clearly evident with a view to the other gas composition spectra in Figure 14. The dominant broad emission at around 82 nm is reduced in favor of distinct VUV transitions from excited species of the minor gas components. A detailed discussion on the results is given in the next two paragraphs.

3.2.2.1 Origin of the VUV Helium Continuum

To understand this behavior, we first need to recognize the nature of the initial intense VUV emission. This spectroscopic feature is known as the *Hopfield continuum*, named after John Hopfield who first reported its discovery in 1930 [63]. It is generated through the transition of an electronically excited state of the bound helium dimer molecule He_2^* to the dissociative electronic ground state. This finding has received much attention and generated interest with respect to fundamental research and the development of strong VUV light sources [64]. At that time such spectroscopic discoveries essentially helped to support and refine the molecular quantum mechanical theories of electronic structures. Furthermore, it was readily discovered that all rare gases can form bound dimers in electronically excited states, which has also drawn considerable practical attention with respect to VUV laser systems since the middle of the last century [65]. An essentially unpopulated, unbound ground state and an abundantly occupied bound electronically excited state form an inverted populated system that can potentially be used for amplified radiation through stimulated emission. Many gas lasers have been realized based on related schemes, in particular the exciplex systems with one rare gas atom and one halogen atom, which show similar bound excited molecule and unbound ground state transitions [66]. Consequently, a vast number of research articles have been published over the years related to the electronic states of the helium molecule and feasible transitions between them. Despite available potential energy curves for the manifold of electronically excited states of He_2^* [67, 68], we put effort in calculating our own set of data, including the nuclear wave functions of each vibronic state. In 2016, Dr. Haack from our group visited the theoretical chemistry group from Prof. Dr. Keiko Takano at the Ochanomizu University, Japan and, among other topics, performed detailed calculations for this project. The potential energy curves presented in Figure 15 were calculated with the Gaussian09 and Gaussian16 software packages [69]. For the ground and the electronically excited states the implemented coupled-cluster (CCSD(T)) and the equation-of-motion coupled-cluster (EOM-CCSD) level of theory, respectively, were applied with the q-aug-cc-pVQZ [8s7p6d5f] basis set by Woon and Dunning [70]. All curves are in excellent agreement with available literature data. The shallow van der

Waals minimum of the ground state $X\ ^1\Sigma_g^+$ at approximately $3.0\ \text{\AA}$ with $9\cdot 10^{-4}\ \text{eV}$ depth reflects perfectly experimental results reported by Burgmans et al. [71]. The energetic order of the excited states at the respective equilibrium position was correctly derived: $a\ ^3\Sigma_u^+ < A\ ^1\Sigma_u^+ < b\ ^3\Pi_g < B\ ^1\Pi_g < c\ ^3\Sigma_g^+ < C\ ^1\Sigma_g^+ < D\ ^1\Sigma_u^+$. Furthermore, the errors for all asymptotes with the separated ground state atom and the respective excited atom are below $2\cdot 10^{-3}\ \text{eV}$, and the errors for the potential minima are below $1\cdot 10^{-2}\ \text{eV}$ as compared to reported values [72]. The errors for the potential barrier heights of the Σ states are below $1\cdot 10^{-1}\ \text{eV}$ as compared to data reported by Guberman et al. [67, 73]. This is a rather good result, considering the difficulties accompanied with such long-range interactions. Consequently, the retrieved set of potential energy curves for the ground and the seven lowest excited states is of high quality. Furthermore, the vibrational levels and the corresponding nuclear wave functions were calculated with the open source WavePacket program [74] and the implemented Fourier Grid Hamiltonian Method [75]. Some of the results are shown in Figure 15 (inset) for the 16 vibrational levels of the $A\ ^1\Sigma_u^+$ state. The two upper quasi-bound levels resulting from the small energy barrier are not considered [76]. In combination with the calculated transition dipole strength for each internuclear distance, the Franck-Condon factors for the wavelength resolved transitions of each vibrational level to the unbound electronic ground state were derived. This allowed to tentatively deconvolute the signatures for the *Hopfield continuum* observed under the various experimental conditions. Thoroughly adjusting the contribution of each vibrational level at the respective wavelength to the overall intensity (cf. Figure 21) yielded approximated relative population distributions. Note that rotational levels were not considered. Carman et al. used a similar approach to reproduce their experimental spectrum by adding the contribution of each ro-vibrational transition to the ground state [76]. However, they assumed a Boltzmann distribution among the energy levels and fitted the theoretical spectrum by adjusting the temperature.

The shape of the remarkable helium continuum, as shown in Figure 14, strongly depends on the specific plasma environment and over the years many explanations for the mechanisms responsible for the different signatures of each individual condition were given [65]. Experiments with high or low pressure and temperature - even liquid helium- and high- or low-energy bombardment with electrons or protons were conducted and analyzed [77-80]. Based on the selection rules, there are theoretically only two possible electronic states with quantum mechanically allowed transitions to the ground state $X\ ^1\Sigma_g^+$ that can explain the observed continuum emission in our work. As depicted in Figure 15 (right), these are the $A\ ^1\Sigma_u^+$ and the $D\ ^1\Sigma_u^+$ each originating from the combination of a ground state helium atom $\text{He}(1\ ^1S)$ with an excited species $\text{He}(2\ ^1S)$ and $\text{He}(2\ ^1P)$, respectively.

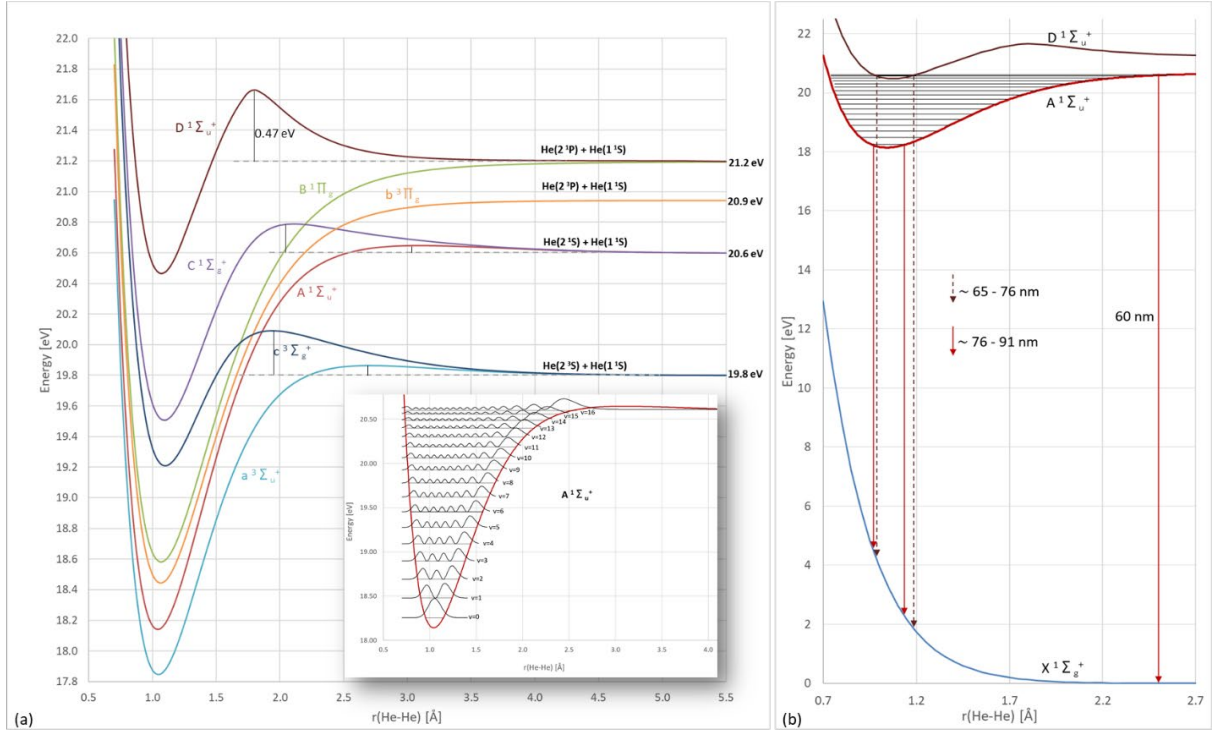


Figure 15 (data calculated by Dr. Haack): (a) Calculated potential energy curves for the ground and the seven lowest excited states of the helium dimer, including the vibrational levels and the corresponding nuclear wave functions of the $A^1\Sigma_u^+$ state. (b) Illustration of transitions from the $A^1\Sigma_u^+$ and the $D^1\Sigma_u^+$ to the ground state $X^1\Sigma_g^+$.

With 20.6 eV, $\text{He}(2^1S)$ is a highly excited metastable atom with radiatively forbidden de-excitation. Approaching a ground state atom can lead to two different molecular states, the $C^1\Sigma_g^+$ and the respective $A^1\Sigma_u^+$ (cf. Figure 15). For both molecules to form - as in virtually any diatomic molecular system - a third partner is required to remove kinetic energy and, in both cases, the mutual approach involves potential energy barriers to overcome [73]. For the $C^1\Sigma_g^+$ we calculated an energy hump of 0.19 eV at 2.1 Å and for the $A^1\Sigma_u^+$ 0.05 eV at 3.1 Å, which relates to gas temperatures of 2205 K and 580 K, respectively. So far, we have not measured or spectroscopically derived exact gas temperatures of the mini spark discharge lamp yet. However, in simple surface measurements of the MS-capillary setup (cf. Figure 1) the temperature never exceeded 340 K during operation. Consequently, it is reasonable to assume that the major fraction of the $\text{He}(2^1S)$ population directly enters the $A^1\Sigma_u^+$ state in first place. Additionally, the small fraction actually forming $C^1\Sigma_g^+$ either through the high energy tail of the Maxwellian distribution or through tunneling effects, will eventually radiate into $A^1\Sigma_u^+$ since this is an allowed transition. The corresponding 0-0 band appears at 913.6 nm [81], however, in our simultaneously recorded UV-VIS-NIR spectra this emission was never observed. Consequently, this strongly supports the assumption of its low population and for the mini spark operated with *pure* helium we expect all generated $\text{He}(2^1S)$ to quantitatively form He_2^* in $A^1\Sigma_u^+$.

In case of $D^1\Sigma_u^+$ we essentially find one other competing state for its formation, since the respective excited $\text{He}(2^1P)$ at 21.2 eV can as well approach a ground state atom to generate the $B^1\Pi_g$ state (cf. Figure 15(a)). The latter does not show any energy barrier at all, which is in stark contrast to the $D^1\Sigma_u^+$ state with a hump at 1.8 Å of 0.47 eV. This relates to a gas kinetic temperature of approximately 5500 K. Hence, the same argument as in the former case applies and excludes significant formation of $D^1\Sigma_u^+$ through this process, but clearly leaves the path into $B^1\Pi_g$ as the more probable one. Note, however, that $\text{He}(2^1P)$ is not a metastable species. In contrast, its coefficient for spontaneous emission to the ground state $\text{He}(1^1S)$ with $A = 1.8 \cdot 10^9 \text{ s}^{-1}$ [61] is significant and suggests a radiative decay rather than a collisional impact upon a single excitation event. Can we nevertheless expect significant formation of $B^1\Pi_g$? The answer is yes. Owing to the radiative trapping mechanism through self-absorption, the lifetime of $\text{He}(2^1P)$ within a dense helium background is significantly enhanced and substantially increases the probability of $B^1\Pi_g$ formation, accordingly [82]. In fact, this reasoning is strongly supported by the recorded spectra (cf. Figure 13 and Figure 14) in which the expected corresponding emission line at 58.4 nm (21.2 eV) is virtually absent. Therefore, it is reasonable to assume that a certain $\text{He}(2^1P)$ population is quantitatively converted into the molecular state $B^1\Pi_g$. As mentioned before, this state is not directly coupled to the ground state $X^1\Sigma_g^+$ to contribute to the VUV continuum. However, the selection rules readily allow the transition to $A^1\Sigma_u^+$ and it is reasonable to expect the depletion of the entire $B^1\Pi_g$ population in favor of $A^1\Sigma_u^+$. Owing to the emission in the infrared region, with the 0-0 band at 2860 nm [83], we were not able to verify this process with our spectroscopic setup yet.

As depicted in Figure 15, several molecular triplet states in close vicinity to $A^1\Sigma_u^+$ - $a^3\Sigma_u^+$, $c^3\Sigma_g^+$, $b^3\Pi_g$ - can and will form. As will be shown further down in chapter 3.2.2.4, the population of the respective atomic species 2^3S and 2^3P is clearly proven through transitions from higher states as observed in the UV-VIS-NIR spectrum. Owing to the forbidden spin conversion, neither the atomic nor the molecular species can radiatively contribute to the VUV continuum directly [84, 85]. Only the interaction of free electrons in the plasma with the excited triplet states can change their spins to singlets and from there proceed as discussed [86, 87]. Despite this mechanism, a large fraction of He_2^* in metastable triplet states is expected and its contribution to the plasma dynamics will be discussed in 3.2.2.4. Furthermore, electron-ion recombination will play a pivotal role in the plasma dynamics and the VUV emission as well. Note that He^+ immediately forms the stable molecule He_2^+ [88] in the experimentally considered pressure regimes applied in the present work. Therefore, electron-ion recombination is essentially a process with the molecular ion and predominantly leads to dissociation - via *dissociative recombination* -

into electronically excited atomic neutral He* in either singlet or triplet states [88, 89]. Those follow the path as discussed and, in case of the singlets, additionally contribute to the VUV emission through the $A\ ^1\Sigma_u^+$ state.

In conclusion, it is reasonable to assume that for the mini spark discharge conditions in pure helium only the transitions from the various vibrational states of $A\ ^1\Sigma_u^+$ to the ground state contribute to the observed continuum (cf. Figure 14). This electronic molecular state is eventually populated by all atomic excited singlet states. Those are either directly or indirectly generated through secondary processes such as from dissociative charge recombination of He₂⁺ or, with minor probability, from triplet conversion with free electrons.

3.2.2.2 Helium Emission in the Presence of a Second Gas Component

As mentioned before, Figure 14 shows some of the VUV spectra recorded by the former PhD student Sebastian Klotowski, which were presented at the ASMS conference in 2014 [62]. The top helium spectrum is of the highest purity we were able to acquire with our present setup, methods and procedures. Despite particular precautions, contributions from atomic nitrogen, oxygen and hydrogen emission, the latter owing to the presence of residual water are present. A list of assigned peaks is given in Table 1.

Table 1: Assignment of experimentally observed emission lines from spectra shown in Figure 14. Data of the involved levels are taken from [61].

species	wvl. [nm]	transition				species	wvl. [nm]	transition			
Ne I	73.6	2s ² 2p ⁵ 3s	² [1/2] ^o	–	2s ² 2p ⁶	¹ S	Xe II	80	5s ² 5p ⁴ 5d	–	5s ² 5p ⁵
Ne I	74.4	2s ² 2p ⁵ 3s	² [3/2] ^o	–	2s ² 2p ⁶	¹ S	Xe II	91.2	5s ² 5p ⁴ 6s	² [2] _{5/2}	– 5s ² 5p ⁵ ² P _{3/2}
Ar II	67.1	3s ² 3p ⁴ 4s	² D _{5/2}	–	3s ² 3p ⁵	² P _{3/2}	Xe II	93.5	5s ² 5p ⁴ 6s	² [1] _{1/2}	– 5s ² 5p ⁵ ² P _{3/2}
Ar II	72.3	3s ² 3p ⁴ 4s	² P _{3/2}	–	3s ² 3p ⁵	² P _{3/2}	Xe II	97-98	5s ² 5p ⁴ 6s	–	5s ² 5p ⁵
Ar II	92.0	3s3p ⁶	² P _{3/2}	–	3s ² 3p ⁵	² S _{1/2}	Xe II	104	5s ² 5p ⁴ 5d	–	5s ² 5p ⁵
Ar I	86.7	3s ² 3p ⁵ 3d	² [3/2] ^o	–	3s ² 3p ⁶	¹ S	Xe II	106.7	5s ² 5p ⁴ 5d	² [1] _{1/2}	– 5s ² 5p ⁵ ² P _{1/2}
Ar I	89.4	3s ² 3p ⁵ 3d	² [1/2] ^o	–	3s ² 3p ⁶	¹ S	Xe II	118.3	5s ² 5p ⁴ 6s	² [2] _{3/2}	– 5s ² 5p ⁵ ² P _{1/2}
Ar I	104.8	3s ² 3p ⁵ 4s	² [1/2] ^o	–	3s ² 3p ⁶	¹ S	Xe I	129.6	5s ² 5p ⁵ 6s	² [1/2] ^o	– 5s ² 5p ⁶ ¹ S
Ar I	106.7	3s ² 3p ⁵ 4s	² [3/2] ^o	–	3s ² 3p ⁶	¹ S	Xe I	146.9	5s ² 5p ⁵ 6s	² [3/2] ^o	– 5s ² 5p ⁶ ¹ S
Kr II	68.5	4s ² 4p ⁴ 5s	² S _{1/2}	–	4s ² 4p ⁵	² P _{3/2}	O I	98.8	2s ² 2p ³ 3s	³ D ₃	– 2s ² 2p ⁴ ³ P ₂
Kr II	78.2	4s ² 4p ⁴ 5s	² D _{5/2}	–	4s ² 4p ⁵	² P _{3/2}	O I	130	2s ² 2p ³ 3s	³ S	– 2s ² 2p ⁴ ³ P
Kr II	82.0	4s ² 4p ⁴ 5s	² P _{1/2}	–	4s ² 4p ⁵	² P _{3/2}	N I	113.4	2s2p ⁴	⁴ P	– 2s ² 2p ³ ⁴ S _{3/2}
Kr II	84.4	4s ² 4p ⁴ 5s	² P _{3/2}	–	4s ² 4p ⁵	² P _{3/2}	N I	119.9	2s ² 2p ² 3s	⁴ P _{5/2}	– 2s ² 2p ³ ⁴ S _{3/2}
Kr II	86.4	4s ² 4p ⁴ 5s	² P _{1/2}	–	4s ² 4p ⁵	² P _{1/2}	N I	149.2	2s ² 2p ² 3s	² P _{1/2}	– 2s ² 2p ³ ² D _{5/2}
Kr II	88.6	4s ² 4p ⁴ 5s	⁴ P _{5/2}	–	4s ² 4p ⁵	² P _{3/2}	N I	174.2	2s ² 2p ² 3s	² P _{3/2}	– 2s ² 2p ³ ² P _{3/2}
Kr II	91.1	4s ² 4p ⁴ 5s	⁴ P _{3/2}	–	4s ² 4p ⁵	² P _{1/2}	H I	102.5	3(s,p,d)	–	1s
Kr I	116.5	4s ² 4p ⁵ 5s	² [1/2] ^o	–	4s ² 4p ⁶	¹ S	H I	121.5	2(s,p)	–	1s
Kr I	123.6	4s ² 4p ⁵ 5s	² [3/2] ^o	–	4s ² 4p ⁶	¹ S					

At 98.8 and 130 nm we observed two oxygen lines, both ascribed to transitions from the $2s^2 2p^2 3s$ electron configuration to the ground state. Thus, in each case one p electron was

excited to the s orbital of the next higher quantum number, resulting in several distinct energetic levels. Deconvolution of three possible transitions closely centered around 130 nm was not possible owing to the limited resolution, and only the unity wavelength is given instead. The VUV contribution of both peaks accounts to approximately 0.5 and 1.5 % relative to the area of the Hopfield continuum. Similar results were obtained with the nitrogen impurity. Again, the most prominent peaks (119.9, 149.2 and 174.4 nm) are assigned to transitions from the relaxation of one electron from the s orbital of the next higher quantum number back to the p orbital of the ground state. The relative emission intensity as compared to the He_2^* is 1.4, 1.7 and 0.7 %, respectively. At 113.4 nm nitrogen shows a line with 1.2 % relative emission, which is attributed to one of the $2s$ electrons relaxing back from the $2p$ excitation into the ground state. The two observed hydrogen lines with 0.2 and 1.7 % relative intensities are readily assigned to the Lyman- β and Lyman- α lines with 102.5 and 121.5 nm, respectively.

Additives: Neon, Argon, Krypton, Xenon

In the following experiments neon, argon, krypton and xenon were successively added to the helium gas flow with mixing ratios up to the percent range at total pressures of approximately 1030 mbar. Figure 14 depicts the changes in the VUV emission in the presence of 0.4 % of the respective heavier rare gas and Table 1 lists the observed peaks with the assigned transitions. A strikingly common characteristic is the dominance of the two transitions from the $(n+1)s$ electron configuration to the $(n)p$ ground state of the respective rare gas, similar to nitrogen and oxygen. Note, that in case of neon the two transitions have merged into one peak at approximately 74 nm, which is also seen in the overlapping 2nd order of the grating at 148 nm, respectively. In principle, the excited $(n)s^2(n)p^5(n+1)s$ electron configuration generates four energetically separated levels, of which only two obey the selection rule for radiative decay into the $^1S_0$ ground state. From the observed intense atomic line emission, for each minor gas component we can expect an abundant population of excited species with one electron in the s orbital of the next higher principle quantum number. It is clearly evident that excimer formation of the minor rare gas components is absent. Again, at the applied high pressures, virtually all *pure rare gas* plasmas - not only helium - show excited dimer formation (He_2^* , Ne_2^* , Ar_2^* , Kr_2^* , Xe_2^*) and for states obeying the selection rules, the respective subsequent intense radiative decay in the vacuum ultraviolet [66, 90] is clearly present. Moreover, the expected VUV line emission of the excited atoms is quantitatively suppressed at these conditions. Figure 16 remarkably contrasts the argon dimer emission (Ar_2^*) and the characteristic argon line emission (Ar^*), both recorded with the spark discharge at atmospheric pressure with pure argon and with 4 % argon in helium, respectively. The

results from Figure 14 and also from Figure 16 suggest dimer formation of the minor component with up to 0.4 % and even 4 % in helium atmosphere to be a negligible reaction path. From a purely application perspective, this behavior readily provides a high pressure, tunable VUV photon source with characteristic line emission.

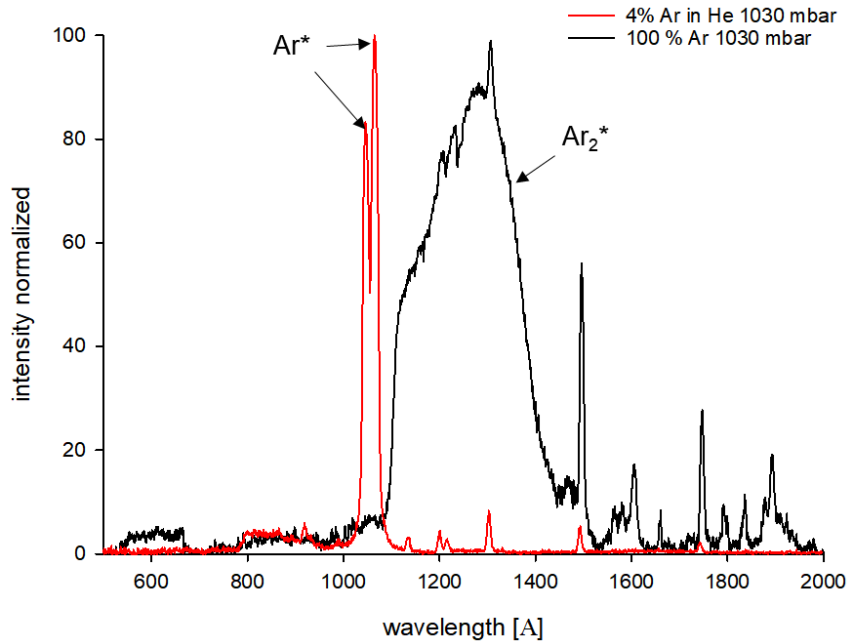


Figure 16 (data recorded by Mr. Winkelmann [7]): Comparison of a spark discharge operated with 100 % argon and 4 % argon in helium, respectively.

Despite the discussed common features for all admixtures, there are also fundamental differences among the spectra shown in Figure 14. Most striking is the considerably different impact on the Hopfield continuum, though exactly the same conditions and mixing ratios were applied. With increasing atomic number, the fraction of the He_2^* emission is significantly reduced and peaks from ionized states of the minor gas component are detected. In case of 0.4 % neon addition to the helium spark discharge, the Hopfield continuum is reduced by approximately 40 %, however, transitions from the ionized state $\text{Ne}(\text{II})$ are not observed. Interestingly, for the same gas concentration of argon, krypton and xenon the continuum is reduced to roughly 70, 75 and 80 %, respectively, and transitions from ionized states are clearly present. Considering the listed wavelength of the (II) states in Table 1, we can reason that some species must have gained substantial energy. In case of $\text{Ar}(\text{II})$ at 67.1 nm (18.5 eV), once more the relaxation of an electron from the s orbital of the next higher quantum number back to the p orbital of the electronic ground state is responsible for the observed emission. However, in this case the electronic ground state is the ion. Consequently, there must be a mechanism driving neutral argon atoms to gain the ionization energy of 15.8 eV plus at least 18.5 eV for the observed transition - in total 34.3 eV. This mechanism does not seem to be amenable for neon, because $\text{Ne}(\text{II})$ lines are not observed. Moreover, a comparison of the

spectra in Figure 14 clearly shows that all the impurity lines seem to be unaffected by neon addition, which is in stark contrast to the other three rare gas compositions with drastically decreased contribution of O(I), N(I) and H(I) by approximately 80 %. All these observations clearly suggest different reaction pathways in the plasma dynamics for neon and the other rare gases, which need further explanation and discussion. At this point, we should remind ourselves that the spectroscopist is only allowed to get a glimpse of the rich plasma dynamics and only a small fraction of the complex chemistry and energy transfer processes is made “visible”.

Returning to the Ar(II) example mentioned above, a total energy gain for a neutral atom of at least 34.3 eV seems possible, because we clearly observed the corresponding transition of the ionized state. With a general introduction to the breakdown dynamics in sections 2.1.1.3 and 2.1.1.4, we have thoroughly discussed the electron energy distribution and the respective energy loss processes during the spark event and have to conclude that this amount of energy cannot be provide to a sufficient degree within a single step. Therefore, this energy has to be transferred in at least two consecutive steps. For a significant fraction of argon atoms, it is reasonable to assume the ionization to the electronic ground state of the ion to be the first step. Again, sections 2.1.1.3 and 2.1.1.4 provided the necessary theoretical background for the fundamental principles. Figure 4 showed the fraction of electron energy loss processes in dependence of the reduced field strength. For pure gases, the electronic excitation into the various energetic states clearly dominate over ionization within the operational regime of the mini spark. With the addition of a second gas of considerably lower ionization energy, the degree of ionization was seen to exceed the excitation curve. However, applied to the considered He-(0.4 %)Ar system, this is *not* the result of a more favorable ionization efficiency between the added argon atoms and the primary electron current. Predominantly, the kinetic energy of the electrons will still excite the various electronic levels of helium, amongst which a considerable fraction is either metastable or radiatively trapped, as discussed in section 3.2.2.1. Only in a second step, these highly excited neutral helium atoms will extensively generate Ar⁺ either through *photo-* or *Penning ionization* (cf. 2.1.1.4). In addition, charge transfer from He⁺ ($IE = 24.6$ eV), or even more probable He₂⁺ (22.2 eV) to argon should not be neglected. Consequently, under these conditions and with these processes in mind, the degree of ionized argon is expected to exceed the corresponding degree of ionized helium atoms by orders of magnitude. In fact, this is paramount to render the 67.1 nm emission amenable to the spectroscopist. The subsequent excitation step from Ar⁺ to an appreciable Ar(II)* population with at least 18.5 eV has to be very efficient. Again, only excited helium species are responsible also for this second energy transfer step. Reasoning from the same arguments applied to the Ar⁺ formation virtually excludes the direct interaction of the primary electron current for this excitation process. However, the

primary electrons can rapidly recombine with the Ar^+ population and the argon excitation can start all over again. This kinetic cycle enhances the efficient He_2^* depletion. To conclude, we validly hypothesize that the vast population of excited neutral helium species in the spark discharge is responsible for (i) abundant ionized argon and (ii) its subsequent efficient electronic excitation.

With these basic concepts and assumptions in mind we can readily explain some of the discussed experimental observations. A glimpse at the potential energy curves in Figure 15 shows that all relevant excited atomic as well as molecular states of helium exceed the ionization energy of argon. This means, neutral argon efficiently depletes these He^* and He_2^* populations. Of course, this also applies to the states $A\ ^1\Sigma_u^+$ and $B\ ^1\Pi_g$, which are responsible for the Hopfield continuum (cf. 3.2.2.1). Any additional kinetic pathway for the degradation of these two molecular and the respective atomic excited states - apart from radiation - effectively reduce the observed VUV continuum, which is in accord with the experimental results. It is anticipated that the entire Ar^+ population is further available for the second energy transfer step, which again consumes excited helium species. In case of the 67.1 nm (18.5 eV) line the $A\ ^1\Sigma_u^+$ in its vibrational ground state (18.3 eV) cannot be depleted for the required energy transfer to the excited $\text{Ar}(\text{II})$, however, in case of the 92.0 nm (13.5 eV) and the 72.3 nm (17.2 eV) transition this is clearly possible (cf. Figure 15). Note, that all three $\text{Ar}(\text{II})$ states are readily excited with the atomic precursor $\text{He}(2\ ^1S)$, though. This is in accordance with the experimental result of roughly 70 % less radiation at 82 nm with the He-Ar system as compared to the pure helium spectrum. Exactly the same arguments apply for the He-Kr and He-Xe mixtures.

With regard to the He-Ne system the process is considerably different. Owing to the rather high ionization energy of neon ($IE = 21.6\text{ eV}$), Penning Ionization cannot occur through the molecular nor the atomic electronically excited states of helium (cf. Figure 15) and an appreciable Ne^+ population is not expected. Consequently, the outlined ionic pathway for efficient depletion of the radiating molecular state of helium is unavailable, which readily explains the absence of any $\text{Ne}(\text{II})$ transition in the spectrum. As listed in Table 1 and shown in Figure 14 and Figure 15, the observed energy transfer from $\text{He}_{(2)}^*$ is to the neutral $2s^22p^53s$ and $2s^22p^53p$ electron configurations with 16.6 eV and 18.4 eV as the lowest states, respectively, and the eventual emission at 74 nm. This concept rationalizes the significantly different impact of neon on the Hopfield continuum as compared to the heavier rare gases (cf. Figure 14). Furthermore, the suppression of impurity emission [$\text{N}(\text{I})$, $\text{O}(\text{I})$, $\text{H}(\text{I})$] is in full accord with the discussed mechanism. As we saw for the neon addition, these spectroscopic features are virtually unaffected, owing to the missing ionic pathway once again. The plasma chemistry for the Ar, Kr and Xe mixtures includes this kinetic route and effectively suppresses the energy transfer from excited neutral helium to residual nitrogen, oxygen and water. Similar observations were made, e.g., by

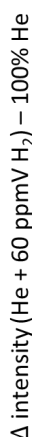
Efthimiopoulos et al. [91]. In the next section, evidence will be given for this mechanism to occur also in the UV-VIS-NIR spectral range.

Additives/Traces: Hydrogen, Nitrogen, Oxygen

In the following, most of the work presented was done by Sebastian Winkelmann as part of his master thesis in 2015 [7] and presented at the 22nd International Symposium on Plasma Chemistry (ISPC) [18]. Mr. Winkelmann continued to systematically investigate the spectroscopic impact of additives to the helium mini spark discharge with a focus on hydrogen and oxygen. In contrast to the rare gases, the mixing ratios had to be significantly reduced down to the ppmV range, in order to reasonably trace any changes in the VUV region. At slightly higher partial pressures, the dimer emission rapidly vanished. To attain such low dilutions, gas cylinders with 1 % of the respective additive in helium were premixed. As exemplarily shown in Figure 17, Mr. Winkelmann also systematically recorded the VUV as well as the UV-VIS-NIR emission for each specific plasma condition. To the best of our knowledge, not many spectra covering the entire range from 50 to 1 100 nm for the same plasma condition are available in the literature. For many plasma scientists, however, a database covering such an extended spectral range is of great value, since it enables predictions for VUV emissions derived from the experimentally much easier accessible UV-VIS-NIR regime. Arranging an optical fiber in close vicinity to the plasma zone is technically very simple and quickly prepared - even spatially resolved - in stark contrast to the experimentally demanding vacuum system and precise plasma alignment required for VUV information.

In addition, both regions provide essentially complementary data on excited species, which are pivotal for fundamental insights into the physical and chemical plasma condition and dynamics. Section 3.2.3 illustrates our continuing work for setting up such a freely available online database.

The top part of Figure 17 depicts a difference spectrum from 50 to 1 100 nm of a discharge with pure helium and with 60 ppmV hydrogen added at 1 030 mbar. Prior to subtraction, the VUV und UV-VIS-NIR data were normalized and combined to the respective single spectrum. No correction was made for absolute photon fluxes considering the wavelength dependent efficiency function of each spectrometer. Therefore, the relative intensities of region 1 (VUV data) are not comparable to regions 2-4 (UV-VIS-NIR data), and also within the same spectral range, intensity information is only partially conclusive. Nevertheless, the difference representation in Figure 17 provides a clear view on the spectroscopic changes upon 60 ppmV hydrogen addition, with positive and negative intensities indicating the increase and decrease of the respective peak intensities.



The four lower spectra depict enlarged views of the marked regions. In general, the peak manifold is far less congested as compared to other plasma conditions. As expected, the emission of the hydrogen Lyman- α line at 121.6 nm with the $2n-1n$ transition clearly increases and dominates region 1. The Lyman- β line with $3n-1n$ transitions at 102.6 nm is visible, however, significantly less intense, which is readily explained by less populated $3n$ states and by the competing depopulation from $3n$ to $2n$. This depopulation is clearly observed in region 3 at 656.3 nm (Balmer- α line). The Balmer- β line for the $4n-2n$ transition at 486.1 nm is also present, with significantly lower contribution, though. Rather unexpected are the molecular bands of NH around 336, 308 and 325 nm, which

were unambiguously allocated to the $\Delta v = 0$ and $\Delta v = +1$ transitions between the electronic states $A^3\Pi \rightarrow X^3\Sigma^-$ and the $\Delta v = 0$ transitions of $c^1\Pi \rightarrow a^1\Delta$, respectively [92, 93]. In general, these triplet transitions strongly interfere with the 2nd positive band of neutral nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$) at 337 nm [94], however, the latter was not observed with the “pure” helium spark condition at all. Only the prominent N_2^+ emission between the electronic states $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ with the (0,0), (0,1) and (0,2) transitions are present in the helium plasma due to the nitrogen impurity of approximately 10 - 100 ppbV. As can be seen in region 2, these clearly decrease upon 60 ppmV hydrogen addition. Likewise, all peaks in the VUV (region 1) assigned to atomic nitrogen decrease as well. Hence, if any neutral molecular nitrogen contributed to the spectrum at around 337 nm, it is expected to decrease upon H_2 addition, similar to the lines observed for N and N_2^+ , but not to suddenly increase. Consequently, a nitrogen interference at 337 nm can be excluded and the relatively strong signal is only due to considerable NH formation. This finding indicates a remarkably efficient mechanism for its formation, considering the rather low mixing ratios of both precursors N_2 and H_2 . Current research in cooperation with our partners Carl Zeiss SMT GmbH (Oberkochen, Germany), ASML (Veldhoven, The Netherlands) and INP Greifswald (Greifswald, Germany) focuses on the plasma chemistry prevailing in the illuminator unit of EUV (extreme ultraviolet) lithography scanners employed in the semiconductor manufacturing process. These systems operate at hydrogen pressures of 10^{-2} mbar and largely suffer from contamination of hydrogenated volatile molecules induced by the extreme high energy photons (90 eV). In these EUV induced plasmas, NH is an essential precursor for example for the formation of NH_3 . These mechanisms are still of considerable interest.

As stated, in our helium mini sparks with N_2 impurities, we have observed the pronounced first negative band of the ionized nitrogen molecule ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) but not, e.g., the well-known 2nd positive band of neutral nitrogen. Experimental work by Dr. Messler for his Bachelor thesis in 2020 [95] showed several spectra from nitrogen plasmas recorded in a regular electron ionization source of a sector field mass spectrometer². With this setup, he recorded the emission distribution of nitrogen under well-defined electron energies between 15 and 150 eV. These spectra clearly indicated a pronounced energy distribution among excited *ionized* as well as *neutral* nitrogen according to the kinetic energy of the electron current. Consequently, the missing neutral bands are compelling evidence that the primary electron current is not responsible for the nitrogen excitation, instead, secondary energy transfer processes from excited helium species dominate. This was already hypothesized in the above discussion with the argon addition. Again, it seems reasonable that the majority of nitrogen molecules is swiftly converted to ions owing to

² Though done in the realm of Plasma Research these data are not shown in the present work, the interested reader is referred to [95].

the interaction with all the available excited $\text{He}_{(2)}^*$ species. Several of the He_2^* electronic states also (cf. Figure 15) show considerable overlap with the $B\ ^2\Sigma_u^+$ state of N_2^+ , with its vibrational ground level at 18.7 eV [96]. This causes an efficient energy transfer route into the electronically excited state of N_2^+ within a single step and explains the sensitive detection of nitrogen impurities in this spectral region. Recall that in case of argon, the ionization and subsequent electronic excitation in order to observe Ar(II) transitions required a two-step mechanism. Finally, it is reasonable to assume that the majority of the N_2^+ population subsequently undergoes dissociative recombination with electrons to form excited N^* species, which fluoresce to generate the spectral abundance of N(I) in the VUV (cf. Figure 17 – region 1) [97]. In these considerations, we still need to clarify the role of 60 ppmV hydrogen and the observed drastical reduction of any other component present in trace amounts. Figure 17 clearly shows all $\text{N}_{(2)}$, O, C and almost all $\text{He}_{(2)}^*$ related peaks on the negative scale, except the 587.2 nm associated with the $1s3d \rightarrow 1s2p$ transition of helium. As shown for example by Sharp et al. [98], H_2 has several molecular electronic states around the energy band of the He_2^* species (cf. Figure 15), including the electronic ground state of the H_2^+ . It appears to be feasible that a very fast resonant energy transfer from $\text{He}_{(2)}^*$ to H_2 takes place. From a kinetic perspective hydrogen would readily depopulate excited helium species and be the winner in the competitive race of all the trace species present. Consequently, the emission of impurities and all helium related transitions are significantly reduced, as observed experimentally. The mentioned positive increase of the 587.2 nm helium line is rather counterintuitive and not quite well understood yet. Furthermore, the dissociation limits of the potential curves of the excited H_2 species (between 14 and 18 eV) [98] are rather low as compared to the excited states of the helium molecule (cf. Figure 15). Consequently, upon the collisional energy transfer from He_2^* either H_2^+ in its electronic ground state or the neutral dissociation products with one ground state and one excited H^* atom including the respective residual kinetic energy are expected. This is in accord with the experimental finding that molecular bands of hydrogen are completely absent, in contrast to the discussed ionized nitrogen system with dissociation limits of excited N_2^+ states above 24 eV [96]. Finally, the excited H^* atoms fluoresce with the previously discussed emissions in the positive scale of Figure 17.

Mr. Winkelmann also varied the oxygen mixing ratio in the helium spark discharge. Some of these data were presented at the 22nd International Symposium on Plasma Chemistry (ISPC) [18] and are depicted in Figure 18. The first two spectra show the pure helium and a 50 ppmV admixture of oxygen, respectively. For a clearer view on the changes, the bottom spectrum represents the difference spectrum of the first two, with increasing intensities on the positive and decreasing intensities on the negative y-axis. Again, the full spectral range of 50-1100 nm is covered, each (VUV and UV-VIS-NIR) normalized to the respective maximum prior to combining them. In case of 100 % He, the VUV range is

relatively clean with a strong helium dimer emission. Mostly nitrogen contributes to the observed impurities and only two minor lines stem from atomic oxygen transitions (99 and 130 nm). Adding 50 ppmV O₂ drastically changes the VUV output. The He₂^{*} emission is reduced by nearly 90 %, the atomic nitrogen contribution is virtually absent, and five strong neutral atomic oxygen lines dominate this range. The latter are assigned to $3s \rightarrow 2p$ (99, 115 and 130 nm), $4s \rightarrow 2p$ (104 nm) and $3d \rightarrow 2p$ (102 nm) transitions. No conclusions can be drawn with regard to feasible oxygen emission in the overlapping range of the He₂^{*}. Similar changes are observed in the UV-VIS-NIR range. The N₂⁺ band structures of the first negative system completely vanish upon oxygen addition and the helium lines are reduced, however, substantially less than in the VUV. Five prominent neutral atomic oxygen lines at 533, 615, 777, 844 and 927 nm appear. Interestingly, only the 844 nm is within the triplet system and leads to an excited state responsible for the subsequent radiative transition into the triplet ground state, with the strong VUV emission at 130 nm. The other four peaks in the UV-VIS-NIR are due to progressions within a quintet system, which finally end in highly excited metastable ⁵S oxygen atoms at around 9.1 eV, with a spin-forbidden transition into the ground state. Precursors for the 99, 102, 104 and 115 nm lines are located in the infrared region which is not amenable to the present setup. Nevertheless, the rather simple spectroscopy of the UV-VIS-NIR region is indicative for the experimental demanding VUV range and allows for rough estimates of its appearance.

The presence of 844 nm radiation ultimately implies the presence of 130 nm, and vanishing N₂⁺ bands (391 nm) strongly suggest reduced radiation from N transitions in the VUV. Moreover, the intensity of, e.g., the 777 nm line allows the plasma chemist and physicist to derive the density of highly excited metastable oxygen atoms. Again, this emphasizes the importance of an easily accessible spectroscopic database covering the VUV-IR range for several plasma conditions.

In Figure 18 only a weak band of O₂⁺ was observed around 563 nm. Increasing the CCD integration time of the UV-VIS-NIR spectrometer to a 50-fold magnification, clearly revealed the band structure of the $b\ ^4\Sigma_g^- \rightarrow a\ ^4\Pi_u$ system [99]. The question arises as to why, in contrast to nitrogen, O₂ does not show pronounced molecular band structures under these plasma conditions. As discussed earlier, the direct interaction of the electron current with these minor components seems to be negligible. More important is the secondary energy transfer of the primary excited helium species, in particular the molecular states as shown in Figure 15. First of all, the energies of these He₂^{*} states are too high for any collisional excited stable neutral molecule of the minor component, ruling out O₂ transitions. Secondly, the dissociation limits of the O₂⁺ electronic states are energetically higher than in the H₂ system, but still less than for the N₂⁺ states [96].

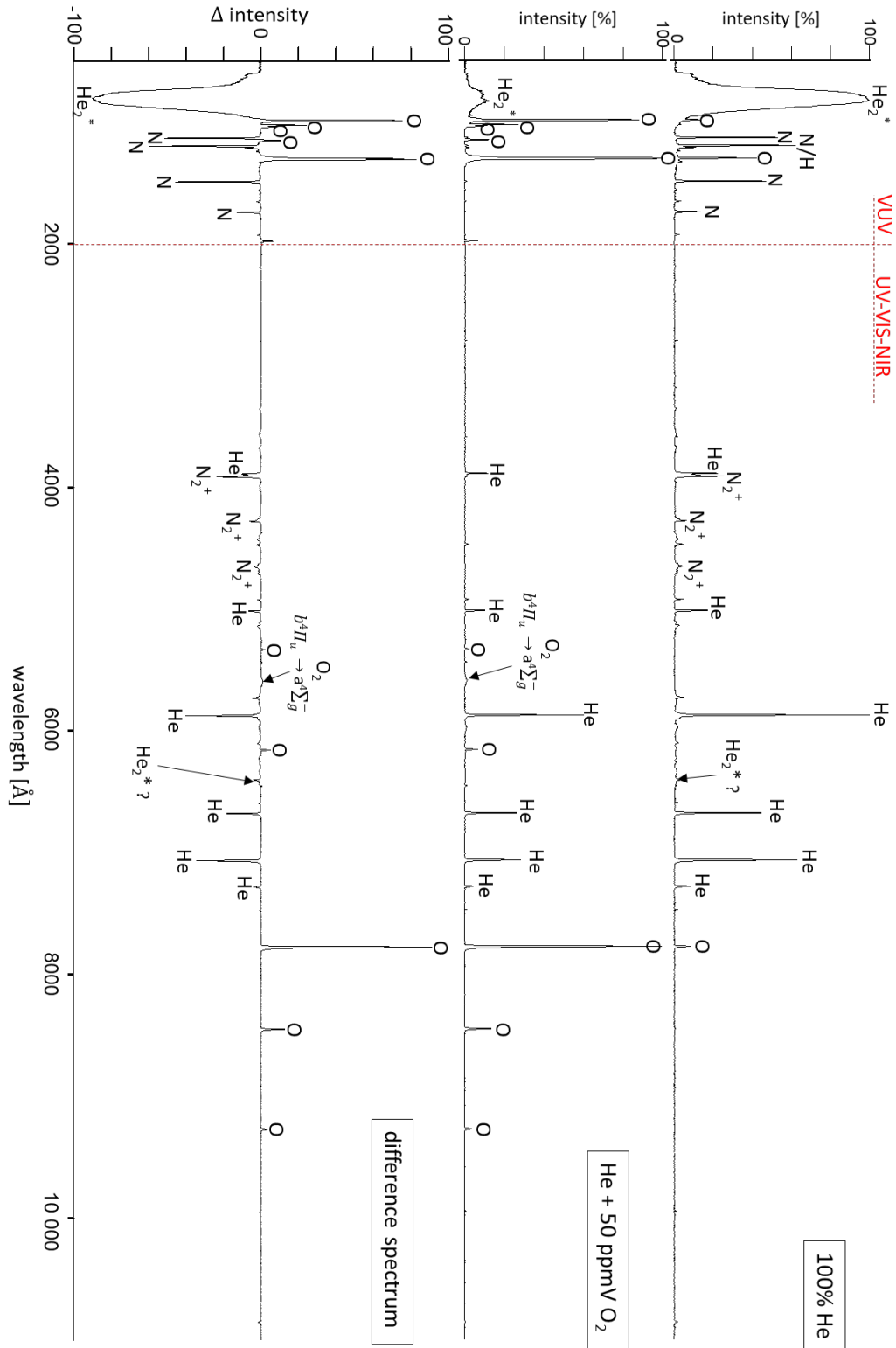


Figure 18(data recorded by Mr. Winkelmann [7]): Spectra from 50 to 1100 nm of a discharge with pure helium and with 50 ppmV oxygen added at 1030 mbar.

Additionally, repulsive, high-Rydberg states, which are also in the vicinity of the excitation region, lead to neutral atomic products (cf. quintet system) as a competing reaction path [100]. Consequently, a certain O₂⁺ population is expected to be present, which is probably

rapidly converted via dissociative recombination to the observed atomic radiating species. However, the O_2^+ population is less pronounced than for nitrogen. To be clear, this does not diminish the quenching efficiency of He_2^* and the impurity contributions through oxygen, it merely explains the virtual absence of O_2 molecular band structures.

One further observation in Figure 18 is worth mentioning. In all our helium discharges, a weak band structure at around 640 nm clearly correlated with the purity of helium and decreased with all added minor gas components, accordingly. This suggests an electronic transition of He_2^* located in the visible region of the spectrum. Compared to work from Li et al. [81] under liquid helium conditions, this spectral feature could result from a $d\ ^3\Sigma_u^+ \rightarrow b\ ^3\Pi_g$ transition, however, an unambiguous assignment was not yet possible. Future experiments with increased resolution and more sensitive equipment will also focus on the UV-VIS-NIR regime for helium dimer emissions. A spectrometer from the Horiba iHR320 series was purchased and a custom software for data acquisition and processing was coded recently. Despite the fundamental perspective of populated states and their chemistry, such band structures in this region would be of great value to also predict the emission below 200 nm in applications with rather difficult direct access to VUV information.

Additives with varying Mixing Ratios

In the following, the variation of the mixing ratios in helium, exemplarily shown for argon and oxygen in Figure 19, is briefly discussed. Note the significantly different dimensions used for each minor gas component, with % and ppmV addition for argon and oxygen, respectively. In fact, this was a general trend observed. For atomic species one to two orders of magnitude higher mixing ratios were required to cause comparable spectroscopic effects in the VUV region as with the used molecular additives.

Furthermore, all additives showed an essentially non-linear behavior between the increasing VUV emission of the additive and the decreasing helium dimer emission. As shown in Figure 19, the intensity of the two argon lines at 104.8 and 106.7 nm are already saturated with 0.7 % mixing ratio, whereas the broad He_2^* radiation still significantly decreases with further addition. The same holds true for oxygen. Here the saturation level of all VUV lines is nearly reached at approximately 20 ppmV, a value at which the dimer emission has decreased by merely 50 %. This non-linearity inherently indicates the existence of a specific maximum mixing ratio with most possible VUV output. This has of course significant practical implications with respect to the brightness of a VUV-photon source. To reveal a more profound mechanistic insight on these remarkable effects, more elaborate experiments will be carried out in the future.

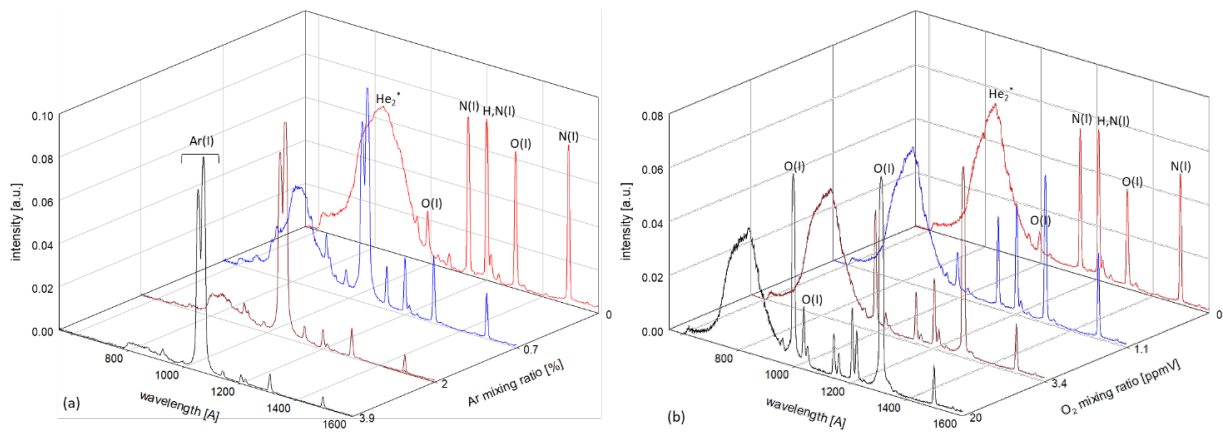


Figure 19 (data recorded by Mr. Winkelmann [7]): Illustration of the differing sensitivity of rare gas and molecular admixtures on the VUV emission of a helium spark discharge. (a) Series of VUV spectra with argon added in the percentage range and (b) series of VUV spectra with oxygen added in the ppmV range.

3.2.2.3 Alteration of the Helium VUV Emission with Pressure

The experimental setup allowed to increase the pressure to approximately 1700 mbar. Settings beyond this upper limit started to lift the spectrometer owing to the flexible hose connection to the gate valve and have not been applied yet. The lower limit was determined by the transition from a spark into a glow discharge at approximately 415 mbar in case of helium. Most pronounced is the pressure effect on the Hopfield continuum in terms of the general shape and width. Figure 20, taken from the final report to the German Research Grant for the project KE 1816 1.1 [2], compares two VUV spectra recorded at 1500 and 415 mbar (a) and depicts the correlation between pressure and the dimer peak width (b).

The fwhm-value nearly follows a linear correlation between 415 and 1700 mbar. Despite noticeable data scattering, the trend is unequivocal and within the recorded range the width increases by almost 8 nm. Figure 20(a) displays the effect on the general shape of the dimer emission. At high pressures, one broad maximum, denoted as the 2nd continuum, is observed. Decreasing the gas density reveals two distinct maxima, denoted as the 1st and 2nd continuum at 60 and 82 nm with a ratio of approximately 1:10 by area, respectively. The position of the 2nd continuum is unaffected by pressure changes, however, a sharp apex forms, which is in stark contrast to the smooth plateau at higher gas densities. Naturally, these effects cannot be rationalized by classical pressure broadening. For a better understanding a closer look at the corresponding potential energy functions is needed. As depicted in Figure 15(b), both continua originate from the same electronic transition $A \ ^1\Sigma_u^+ \rightarrow X \ ^1\Sigma_g^+$, i.e., from the highest and lowest vibrational level of $A \ ^1\Sigma_u^+$. In 1963, Tanaka and Yoshino were the first suggesting this mechanism [77].

Michels et al. proposed an additional contribution from the $D \ ^1\Sigma_u^+ \rightarrow X \ ^1\Sigma_g^+$ transition to explain the Hopfield formation under different plasma conditions [80]. As discussed in section 3.2.2.1, we explicitly excluded significant $D \ ^1\Sigma_u^+$ population in our case for two reasons: (i) The high energy barrier of 0.47 eV for its formation relative to the rather cold plasma and (ii) the more favorable alternative route for the atomic precursors to stabilize in the barrier-free $B \ ^1\Pi_g$ state. Similar to the work of Smith and Meriwether in 1965 [101] and Michels et al. [80] in 1987, we reconstructed the spectral features of the Hopfield continuum by calculating the He-He separation dependent Einstein $A(R)$ -coefficients of all the involved vibrational levels of $A \ ^1\Sigma_u^+$ (cf. Figure 15). In a second step, the vibrational population distribution was manually adjusted as to optimally fit the resulting curve of the summed and scaled $A(R)$ -coefficients with the experimental data at each wavelength increment. In contrast to Michels et al., we considered all 16 vibrational levels to resemble the spectroscopic feature, and not just the first four. It is conceivable that they could have matched their respective data without the need of $D \ ^1\Sigma_u^+$ contributions, by including all vibrational levels of $A \ ^1\Sigma_u^+$ as well.

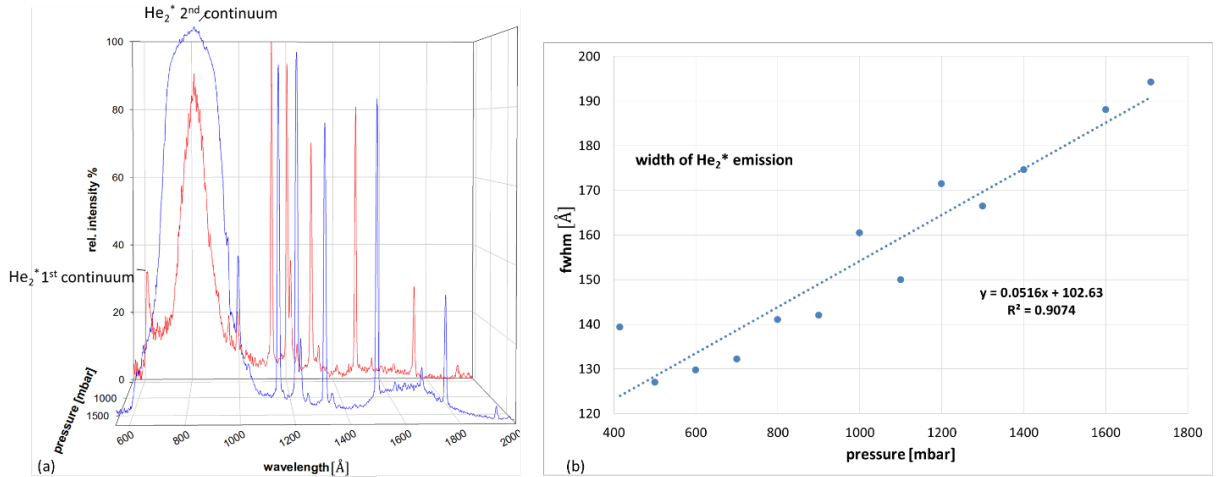


Figure 20 adopted from the final project report (KE 1816 1.1) to the DFG: Illustration of pressure effects on the helium dimer emission from a spark discharge. (a) VUV spectra recorded at 415 mbar and 1500 mbar and (b) correlation between the fwhm-values of the 2nd continuum and the pressure.

The Einstein $A(R)$ -coefficient is directly proportional to the emission intensity and can be calculated from the transition dipole moment d according to [102]:

$$A(R) = \frac{2}{3} \frac{e^2 (2\pi)^3}{\varepsilon_0 h \lambda^3} d^2 \quad (10)$$

with e the elementary charge, ε_0 the vacuum permittivity, h the Planck constant and λ the wavelength. Principally, the transition dipole moment d is a function of the electronic dipole transition moment μ_e and the nuclear wavefunctions of the upper and lower states, $\chi_{n,v''}$ and $\chi_{m,v'}$, respectively. In its numerically integrated form it is commonly written as:

$$d_{n,v'',m,v'} = \sum_i \chi_{n,v''}(R_i) \cdot \mu_e(R_i) \cdot \chi_{m,v'}(R_i) \cdot \Delta R \quad (11)$$

with ΔR as the applied He-He separation increment.

During his stay at the Ochanomizu University, Japan (cf. section 3.2.2.1), Dr. A. Haack calculated all $\chi_{n,v''}(R_i)$ normalized nuclear wavefunctions of the upper state $A^1\Sigma_u^+$ with high precision (cf. Figure 15). Applying the multireference configuration interaction (MRCI) method [103], he also obtained very accurate values for the electronic dipole transition moments μ_e in dependence of R between $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$. Since the lower state is repulsive, a classical, normalized nuclear wavefunction for $\chi_{m,v'}(R_i)$ cannot be obtained. With the concept of the reflection method, however, an approximation for $\chi_{m,v'}(R_i)$ can be derived as follows [104, 105]:

$$\chi_{m,v'}(R_i) = \left(\frac{\Delta E_X(R_i)}{\Delta R} \right)^{-\frac{1}{2}} \quad (12)$$

This expression requires the energy difference ΔE_X between two points along the repulsive ground state potential energy curve with the incremental He-He separation ΔR . With the required input for the transition dipole moment in equation (11) at hand, we were able to calculate the $A(R)$ -coefficients in equation (10) for each vibrational level of $A^1\Sigma_u^+$ with 0.006 Å resolution, for nuclear distances between 0.7 and 4 Å. The vertical energy difference between the upper and lower state at each of these points was translated into the respective wavelength. A manually adjustable scaling factor was used to vary the population distribution among the 16 vibrational levels. In this way we plotted the emission distribution between 59 and 109 nm of each vibrational level and, in addition, the superimposed emission. The latter was adjusted to match the experimental data by varying the population distribution. Results are shown in Figure 21 for two sets of data obtained at 1000 mbar and 415 mbar, respectively. The green lines represent the experimental data, whereas the red lines illustrate the best fit of the calculated superimposed emission distribution values. The dashed curves depict the emission distributions of each individual vibrational level scaled by the respective relative population. The insets in the upper right corners show the population distributions used for the simulated fits.

First of all, the simulated spectra match rather well, which suggests that the employed population distributions are in good accordance with the experimental findings. Slight deviations for longer wavelengths are discernable, however, they are readily explained by the nature of the steep slope of the repulsive curve at smaller nuclear distances.

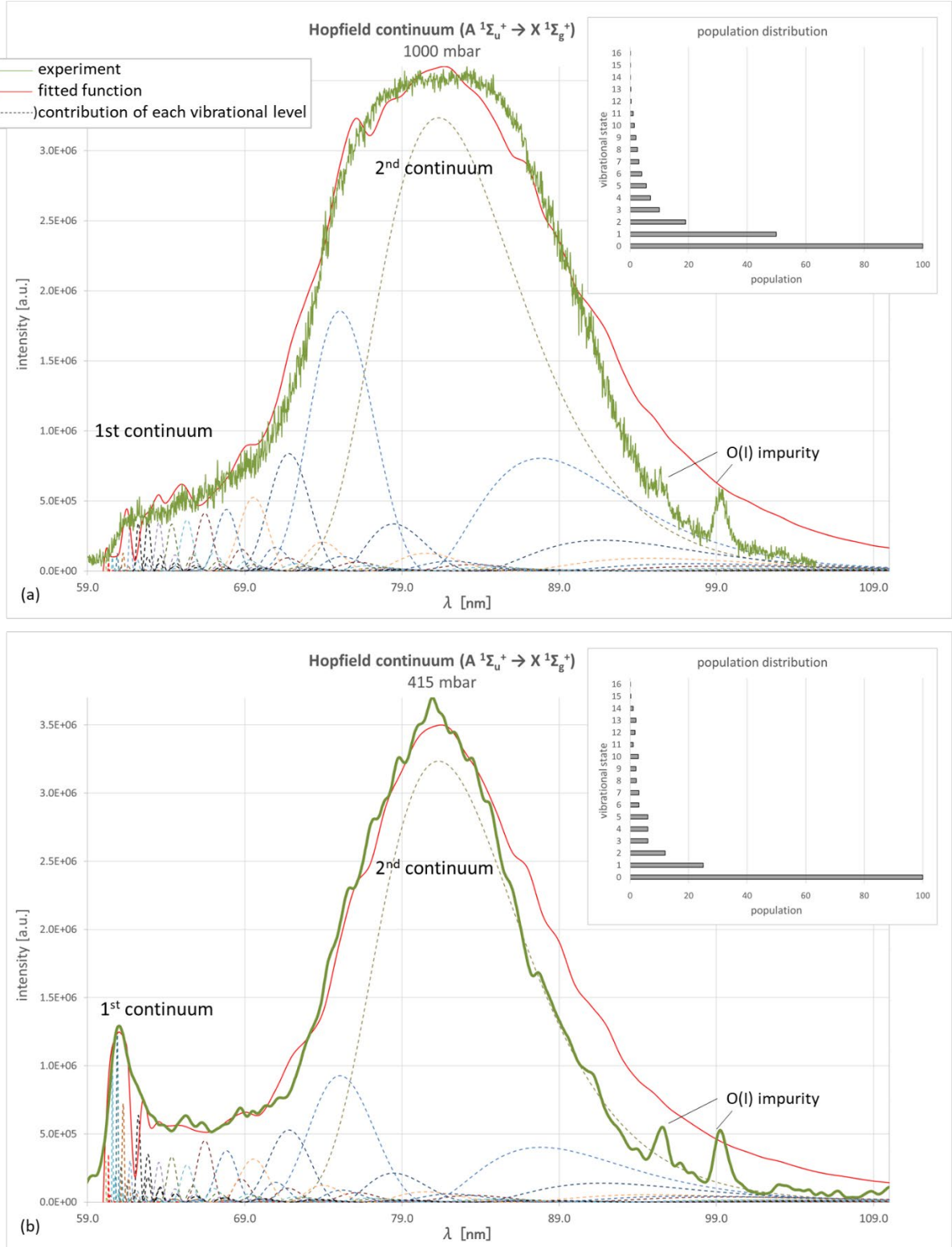


Figure 21: Fitted function to the experimentally recorded helium dimer emission of the 1st and 2nd continuum for pressures at (a) 1000 mbar and (b) 415 mbar. For the fit, the population distribution of all sixteen vibrational levels (cf. Figure 15) were manually adjusted. The calculated vibrational energies and their corresponding nuclear wavefunctions allow to derive a wavelength dependent transition strength to the unbound ground state from each level. An inset within each spectrum displays the resulting vibrational population distribution that matches the fitted function. Additionally, the contribution of each individual vibrational level to the overall function is visualized by the dashed lines within each spectrum.

Transitions to the left side of the potential energy curves essentially determine the shape of the continuum spectrum at these wavelengths (cf. Figure 15). Hence, small errors in

this steep region of the calculated ground state function cause fairly large deviations from the actual emitted photon wavelength. The importance of a carefully determined repulsive potential energy function to describe the Hopfield continuum was already stressed by Tanaka and Yoshino [79] in 1969 and generally holds true for all simulated continuum spectra.

Despite this small discrepancy, we obtained fits with reasonable vibrational population distributions. The spectrum at 1000 mbar shows an exponential decay of the occupation from $v = 0$ up to $v = 16$, closely reflecting a Boltzmann distribution for approximately 3300 K. Clearly, the concept of temperature is not meaningful in this context. Nevertheless, this comparison suggests an equilibrated system between the He_2^* formation in $v = 16$ from one $\text{He}(2^1S)$ and one ground state $\text{He}(1^1S)$, the subsequent collisional de-excitation down to the vibrational ground state $v = 0$ and the radiational lifetime of each vibrational level. In contrast, at 415 mbar a more irregular occupation with a strong dominance of the lowest level is observed. The reason is not quite clear, however, it seems that under this condition the radiational lifetime of certain vibrational levels compete with the collisional deactivation.

With the distributions available, one could in principal proceed and tentatively derive a more comprehensive and quantitative kinetic model, including the rate of $A\ ^1\Sigma_u^+$ ($v = 16$) formation and the rates of vibrational and radiational de-excitation of each individual vibronic level to explain these effects. The probability for a radiative transition into the repulsive ground state is given by the integration of the He-He separation dependent $A(R)$ -coefficient for each level. As mentioned, these were accurately calculated by Dr. Haack for this project. Furthermore, it is reasonable to assume that the recorded spectrum reflects a quasi-steady state distribution, since the time constants for the involved relaxation and de-excitation processes are considerably shorter than the spark pulse. The two great unknowns for this kinetic approach, however, are the excitation frequency of the $\text{He}(2^1S)$ state and more importantly, the specific vibronic relaxation rates. Tolerating a rather large error, the formation of the excited atomic state could be adjusted tentatively. The individual vibrational relaxations of this excited dimer, however, turn out to be rather complex processes that were given particular attention in numerous publications in the second half of the last century with regard to the performance of excimer lasers. In a comprehensive review titled "*Vibrational relaxation of excimers*", Datsyuk et al. [106] summarized the different theoretical approaches that were applied to explain and model excimer/dimer emission spectra under various conditions. The complexity particularly arises from the possibility of multiquanta relaxation steps, i.e., not a simple level-to-level decline, and feasible electron induced relaxation processes.

Unfortunately, for both mechanisms we are currently facing an insufficient data situation in order to derive reliable kinetic models for the He_2^* vibronic population distributions recorded with the spark discharge setup. Moreover, we can hardly estimate the contribution of other molecular electronic states, which are not radiatively coupled to the ground state but can certainly populate specific vibrational levels of $A^1\Sigma_u^+$, [65, 82, 107]. At present, these unknown factors render the outcome of any kinetic approach highly speculative. Nevertheless, further research in this realm with the presented tools at hand remains of significant interest.

3.2.2.4 Alteration of the Helium UV-VIS-NIR Emission with Pressure

Figure 22(a) illustrates the different behavior of the VUV and the UV-VIS-NIR output upon varying pressure. Between 500 and 1 200 mbar the total VUV emission increases linearly by more than a factor of three, whereas the integrated UV-NIR is inversely related with more than halving the intensity. The latter dependency was confirmed by a linear regression in an intensity vs. $1/p$ plot, depicted in Figure 22(b). Virtually all helium lines follow this trend (data not shown). In other words, higher pressures essentially dimmed the spark lamp in the visual region, while simultaneously increasing the flux of ionizing radiation. This is important to consider when optimizing the conditions for a photo ionization lamp, since usually the visual brightness of a plasma is regarded as a measure. Besides practical aspects, this finding is readily explained by the competition between radiative decay and collisional formation of He_2^* . Higher pressures favor dimerization and hence suppress radiative decay in the UV-VIS-NIR between highly excited states. On the other hand, a higher dimer population favors radiation emission in the VUV.

Figure 22(c) breaks down the total emission behavior in the UV-VIS-NIR into the individual population of each radiating helium species at the respective pressure condition. The relative intensities in this plot were normalized to the applied integration times, the respective Einstein A-coefficients for spontaneous emission [61] and to the total UV-VIS-NIR radiation of all helium lines. Assignments of the observed transitions to the involved states and their energies relative to the ground state are listed in Figure 22(d). Most striking is the altering relative population of the $^3S_1$ state responsible for the 706.5 nm emission. Compared to the other helium states, this transition seems to be more sensitive to pressure changes. Its relative population available for radiative decay drops from 30 % to 18 % between 415 and 1 700 mbar, respectively. In other words, this state is more favorably converted to highly excited He_2^* than any other state. The work from Pouvesle [108] partially addresses this issue. However, the reason for this trend at the present operational conditions of the mini spark remains rather speculative at the moment and requires further experimental and theoretical investigations.

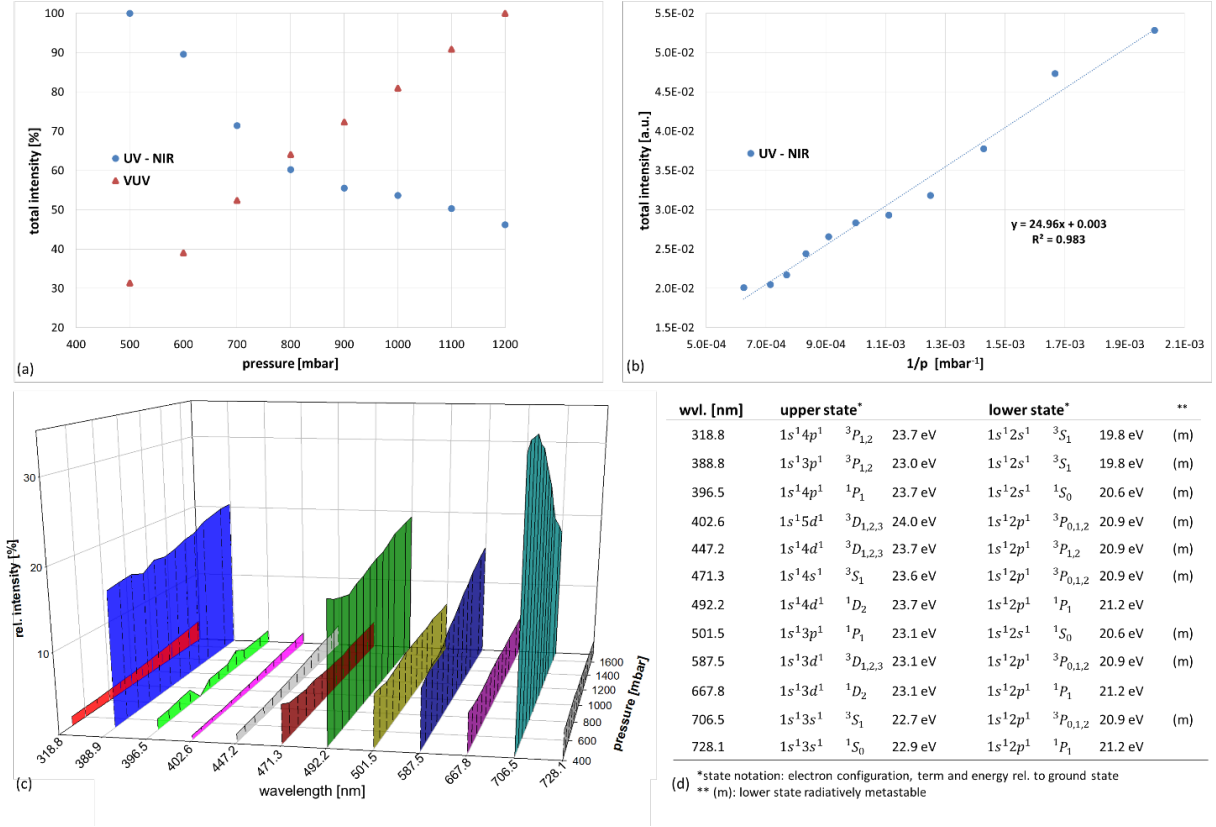


Figure 22 adopted from the final project report (KE 1816 1.1) to the DFG: Illustration of pressure effects on the radiation of a helium spark discharge in the UV-VIS-NIR. (a) Comparison of the pressure dependence of the total intensity in the VUV and UV-VIS-NIR, (b) plot of the total UV-VIS-NIR intensity vs. the inverse of the pressure, (c) intensity of selected wavelengths in dependence of the pressure and (d) table listing the corresponding transitions of the selected wavelengths.

In the list in Figure 22(d), we also see that nine out of twelve observed helium lines terminate in metastable states. Their appearance directly indicate the presence of He_2^* species. However, only the 501.5 nm and the very weak 396.5 nm transitions terminate in $^1S_0$ at 20.6 eV responsible for the $A \ ^1\Sigma_u^+$ formation (cf. Figure 15). Consequently, their emission strength directly relates to the intensity of the Hopfield continuum in the VUV. As seen in Figure 22(c) the intensities of these two lines remain virtually constant throughout the pressure variation and the strong increase of the continuum emission (cf. Figure 21) cannot be explained simply by a higher population of the respective electronically excited atomic precursor. This calls for alternative mechanisms, such as triplet-singlet conversion of He_2^* or more favorable transitions from higher dimer states into $A \ ^1\Sigma_u^+$, in addition to those shown in Figure 15. To examine the latter, we require an extension of the spectroscopic setup into the IR region, in order to follow feasible dimer-dimer transitions between closely spaced potential energy curves as well.

Finally, it is worth noting that three observed transitions in the visible region from the list in Figure 22 (d) terminate in the non-metastable level $^1P_1$ at 21.1 eV. The next lower accessible state via electromagnetic radiation is the ground state and one may expect to see the corresponding 58.4 nm in the VUV spectrum. However, this wavelength has not

been observed throughout our experiments. As pointed out in section 3.2.2.1, the reasons are: First, the competing formation of the $B\ ^1\Pi_g$ molecule (cf. Figure 15) at elevated pressures. The collision frequency at 1000 mbar is close to the Einstein A-coefficient of $1.8 \cdot 10^9\text{ s}^{-1}$ [61] and essentially channels a large portion of the $^1P_1$ atoms immediately into the dimer before fluorescing. The reaction into the $D\ ^1\Sigma_u^+$ was excluded for reasons discussed in detail in section 3.2.2.1 and section 3.2.2.3. The second reason is the radiative trapping, enhancing the lifetime of this energetic level by frequent emission and reabsorption within the collective of the helium matrix. This process favors dimerization, but also leads to large scattering. In our particular experimental procedure, i.e., a 1000 mbar helium matrix, it essentially prevents this 58.4 nm wavelength from being properly diffracted by the grating and subsequently detected by the photo multiplier.

Nevertheless, we unambiguously confirm a significant $^1P_1$ population through the linked transitions in the UV-NIR regime. However, to identify the dimerization contribution to the vanishing 58.4 nm, the additional IR information of the corresponding $B\ ^1\Pi_g \rightarrow A\ ^1\Sigma_u^+$ transitions is required. Once again, this emphasizes the need for a more elaborate spectroscopic setup. It should cover the full range from the VUV to the IR in order to provide a more comprehensive data set for a better elucidation of the prevailing plasma dynamics.

3.2.2.5 Air Spark Discharge

Initiated by presentations of our spectroscopic plasma data obtained with the discussed setup, interest from institutions and companies arose, with requests on recording VUV to NIR full range spectra for various applications. For example in 2015 full range spectra of air spark discharges were recorded for AIRSENSE Analytics GmbH, Germany. As described in section 3.1.1, the custom power supply employed provides voltages up to 1500 V, which is insufficient for air sparks at atmospheric pressure with the regular gap of 0.5 mm. Breakdown was observed starting at approximately 150 mbar, however, with very weak emission intensities. Furthermore, careful preparation of the background gas condition with helium was required to prevent the air sample from diffusing into the spectrometer and essentially absorb the VUV radiation. On the other hand, the helium background should not contribute to the plasma characteristics and falsify the radiation from the air sample. For the spectrum shown in Figure 23, the setup was evacuated to $3 \cdot 10^{-6}$ mbar and rapidly filled with helium to 18 mbar. The in- and outflow from the electrodes, with connections to the air sample and the rough pump, respectively, were carefully adjusted to maintain a final, constant pressure of 19 mbar. Under these conditions NO and N₂ emissions clearly dominate the spectrum with strong features between 200 and 450 nm. Since helium lines are not observed, it seems reasonable that

perturbation of the plasma dynamics through the background gas is negligible. Below 200 nm all atomic lines discussed previously (section 3.2.2.2) are present, however, not as abundant. The entire visible and near infrared region is virtually unpopulated, not even the $b\ ^4\Sigma_g^- \rightarrow a\ ^4\Pi_u$ system of O_2 or the prominent atomic oxygen lines at 777, 844 and 926 nm are observed (cf. Figure 18).

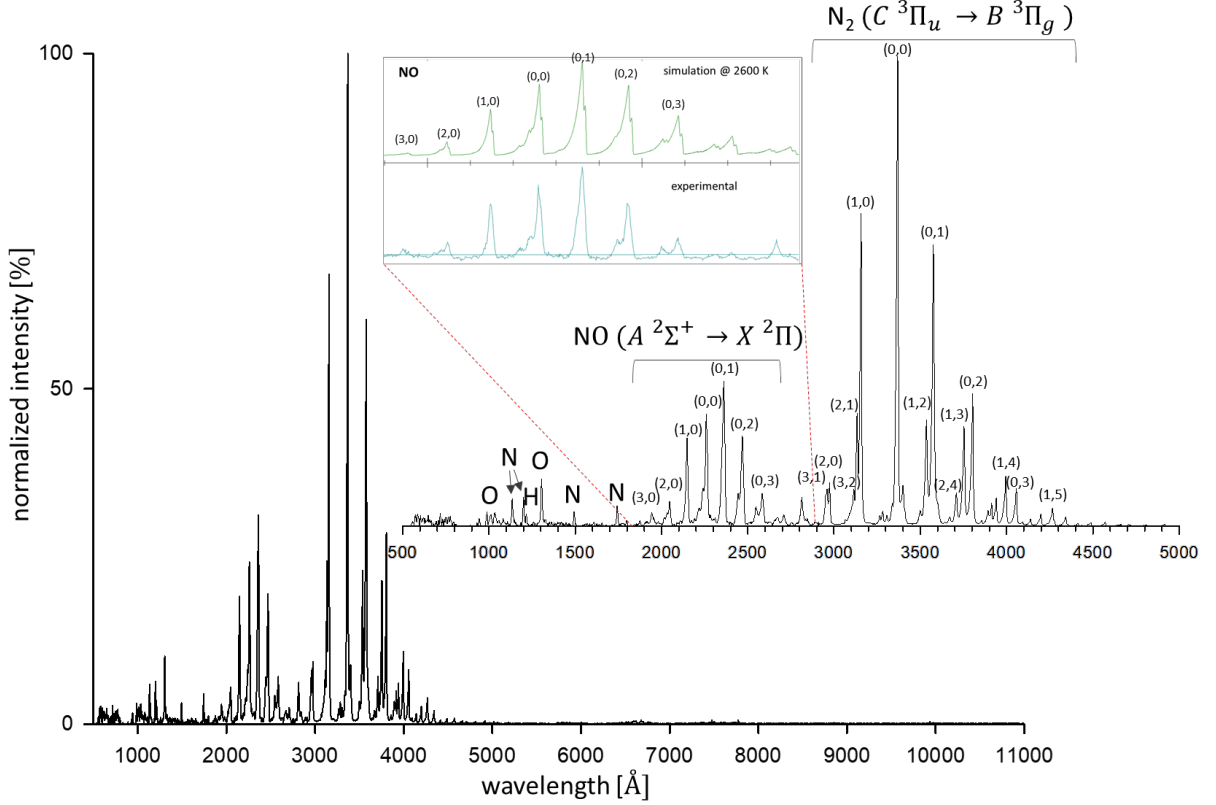


Figure 23: Air discharge at 19 mbar, with helium as background gas. The enlarged region shows the characteristic signatures of NO and N_2 emission.

Protruding is the second positive system $C\ ^3\Pi_u \rightarrow B\ ^3\Pi_g$ of neutral nitrogen, which extends to transitions from the third vibrational level of the upper electronic state. The difference when comparing the spectra with air as an impurity in helium (cf. Figure 17) is remarkable. In case of the air sample the first negative band system of N_2^+ ($B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$) is completely absent and in case of helium as the main gas constituent the exact opposite is true and no neutral nitrogen emission is observed. Detailed spectroscopic measurements of nitrogen inside a conventional electron ionization source as described in section 3.2.2.2 [95] clearly demonstrated a transition between the second positive and the first negative system with increasing electron energy. Consequently, the air spark discharge is governed by a relatively low electron energy distribution that cannot significantly populate electronic states beyond the nitrogen IE threshold of 15.6 eV. On the other hand, the sharp cutoff between these two band systems with N_2 in helium strongly suggests that under these conditions the energetically well-defined

excited helium species are responsible for populating the $B\ ^2\Sigma_u^+$ of nitrogen (18.7 eV) and not the primary electron current.

Comparison of the pronounced NO ($A\ ^2\Sigma^+ \rightarrow X\ ^2\Pi$) signature with a simulation performed with the software package LIFBASE [109] suggests an equilibrated rovibrational temperature of approximately 2600 K (cf. inset in Figure 23). The vibrational excitation clearly results from the chemical reaction forming the NO molecules from electronically and vibrationally excited and partially dissociated N₂ and O₂. Though the kinetic energy distribution of the electrons is deemed low, a large population of N₂ will nevertheless be highly energetic. The observed second positive system with the $B\ ^3\Pi_g$ as the lower state will further radiate in the infrared to the $A\ ^3\Sigma_u^+$ state, which is metastable with respect to the electronic ground state. These species carry an electronic energy as large as 6.2 eV. A more detailed mechanistic study on the NO formation process, however, is not possible with the current data basis. Nevertheless, it is emphasized that plasma induced fixation of nitrogen either via hydrogenation (cf. Figure 17) or the discussed oxygenation is a current topic with a promising and seriously considered alternative route to the Haber-Bosch process [110].

3.2.3 Establishing an Online Spectroscopic Database

The previous chapters essentially attempted to elucidate plasma dynamical effects with spectroscopic information covering the wavelength range 40-1100 nm. The availability of such a broad data set has proven to be extremely useful in this work. Many of the UV-VIS-NIR lines are directly linked to the population of species responsible for the characteristic features in the VUV and vice versa. Only such an extended spectroscopic range covering all the impacting parameters allows to find the necessary puzzle pieces and to reveal the bigger picture of the involved plasma dynamics.

There is no question that a multitude of spectral databases has been established during the last 160 years since the invention of Bunsen and Kirchhoff's spectral analysis [111]. These are the foundation for unambiguous and mostly automated identification of elemental composition in analytical disciplines such as laser induced breakdown spectroscopy (LIBS) or inductively coupled plasma optical emission spectroscopy (ICP-OES), just to name two. However, there is a lack of databases providing "full range" (VUV to NIR) spectra for specific plasma conditions. All the databases available do not tell us the UV-NIR features for one plasma condition and at the same time, how the resulting VUV spectrum may look like.

Consequently, initiated through the DFG grant "miniature spark discharge lamps (KE 1816 1-1)" [2] we launched a freely available, online spectroscopic database, publishing

full range spectra for various spark plasma conditions [5]. Figure 24 depicts a screenshot of the web interface, designed and coded by Dr. Wißdorf, senior scientist at the University of Wuppertal, Physical and Theoretical Chemistry (PTC), to whom I am expressing my sincere gratitude for this work. Slide controls allow the user to interactively change the discharge conditions, such as the pressure or the gas composition and follow the corresponding spectral changes from 40 to 1100 nm in real time. Currently, the data are specific to the miniature spark discharge. Nevertheless, it should give the user and spectroscopist doing research in (near) atmospheric pressure plasmas a general idea of the particular application and provide support for specific interpretation. Particularly for users equipped with only a fiber optical spectrometer operating in the UV-VIS range, this library should enable a data evaluation and then allow a rather good prediction of the corresponding VUV spectrum.

This database is continuously growing with more data and variables to choose from. Moreover, higher resolution spectra will be added covering the UV-VIS-NIR range. In the near future, we also plan an experimental setup, which will provide data covering a considerable part of the IR range as well.

Spectrum Explorer

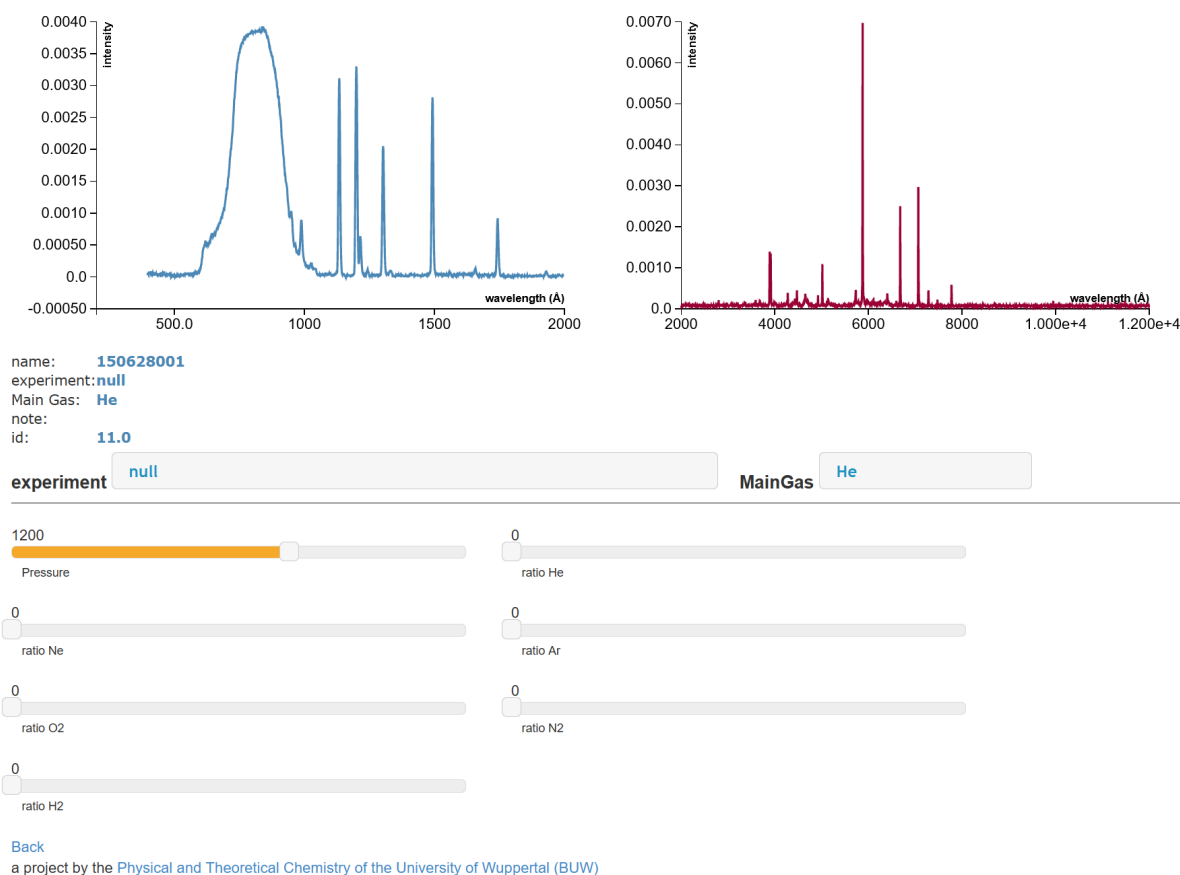


Figure 24 [5]: Picture of the launched online database for spectra recorded with the spark discharge in the range between 40 nm and 1200 nm under various conditions.

3.3 Time Resolved Experiments

3.3.1 Current, Voltage and Emission Characteristics

Most of the results discussed in this chapter have been presented at the 2014 ASMS conference [62]. They were verified again in 2016.

Figure 25 displays the time resolved signals of the recorded voltage, current, VUV and UV-VIS data for an entire discharge cycle. For the data presented, the spark discharge was operated with pure helium at a pressure of 993 mbar, a total gas flow of 350 sccm and an excitation frequency of 1.5 kHz. For details concerning the experimental setup the reader is referred to section 3.1.5.

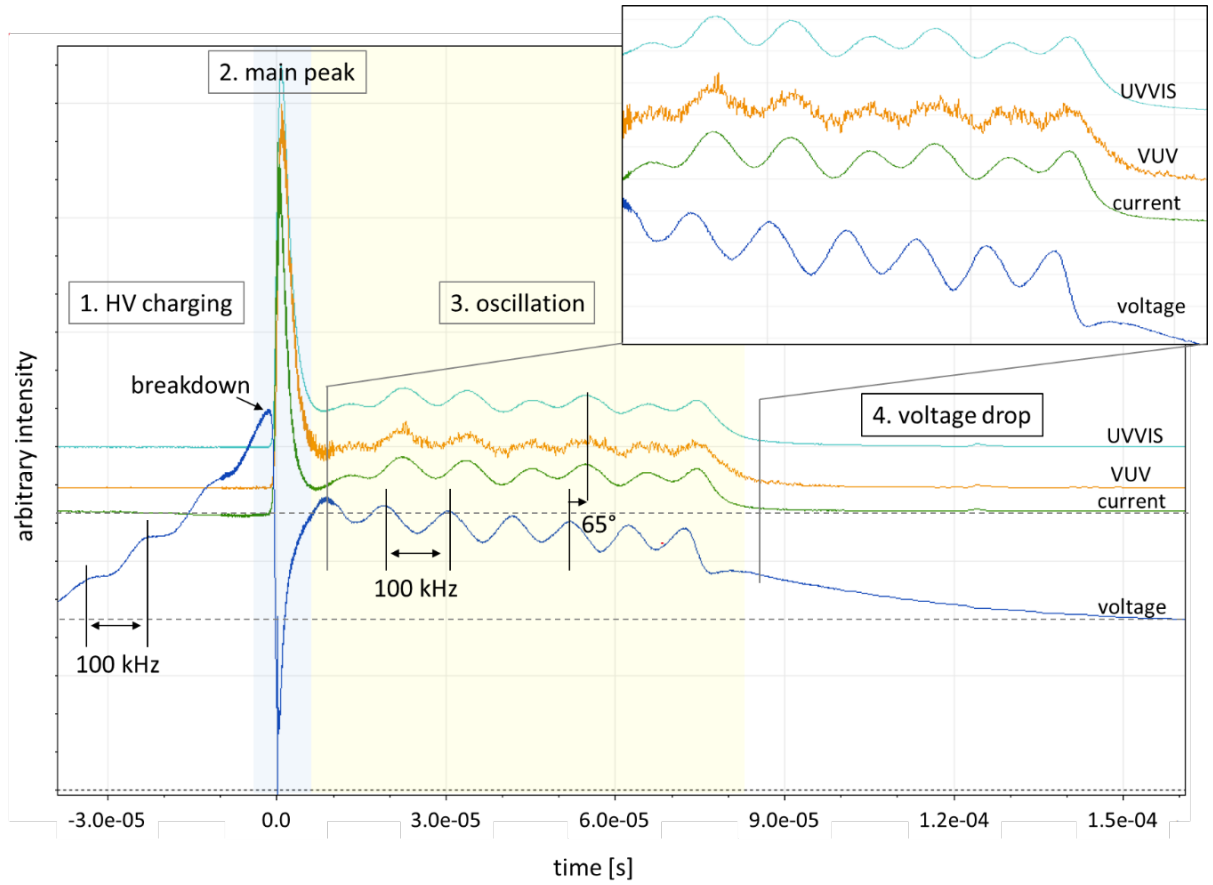


Figure 25: Illustration of the temporal evolution (time sequence) of voltage, current, VUV, and UV-VIS-NIR signals over a single discharge cycle. The data corresponds to a helium spark discharge operated at 993 mbar pressure, 350 sccm total gas flow, and a frequency of 1.5 kHz.

One complete discharge cycle is about 180 μs long and is divided into four phases: (i) The *HV charging* for approximately 30 μs , (ii) the breakdown with a short and intense *main peak* lasting for about 1.5 μs , (iii) a subsequent *oscillation* of 75 μs and (iv) a final *voltage drop* for 75 μs . It has been certified that all signals and oscillations are genuine from the sparking circuit and are not induced by interferences or noise of the diagnostic setup. In the first phase the two 1 nF capacitors are charged and the voltage recorded between anode and ground increases accordingly (cf. Figure 12). A superimposed ringing of approximately 100 kHz is notable, which is in good agreement with the operation

frequency of the switch mode supply. The current recorded on the cathode relative to ground is virtually unaffected during this phase, only a minor superimposed ringing of the same frequency as for the voltage is observed (only seen in enlarged representation). As expected, both light emission related signals show no response throughout the charging period at all. Upon breakdown, the main peaks in all four recordings evolve as strong and sharp signals within approximately $0.5\ \mu\text{s}$ and last for another 0.5 up to $1\ \mu\text{s}$. Two further observations can be made: First, the peak maxima of all four slopes essentially occur at the same time and secondly, the voltage signal is inverted. Both effects are attributed to large space charge clouds generated in the vicinity of each electrode, which effectively drive the entire discharge dynamics in this time domain. Further explanations on the nature of the main peak and in particular its dependence on the prevailing pressure are assessed in the next section (cf. 3.3.2).

Several aspects of the subsequent oscillation phase are worth a closer inspection. In the voltage recording, seven cycles of virtually the same amplitude and with identical frequency as for the charging phase are observed and the waveform is not inverted. After the last cycle the ringing suddenly stops. Furthermore, these oscillations appear superimposed on a general underlying exponential decay of the voltage slope with a mean level at half the breakdown voltage. The temporal response of the other three recorded parameters are remarkable as well. The VUV and the UV-VIS-NIR waveforms exactly match the current signal. Again, this was verified several times with different setups to exclude any interference artefacts. At $100\ \text{kHz}$, essentially the identical frequency and also the same number of maxima as for the voltage is determined, however, with a phase shift of 65° . This strongly differs from the main peak behavior. At the end of this region all three quantities dropped to their respective ground level as in the charging domain. In contrast, the voltage still continues to decrease in the fourth phase to the respective ground level in between two consecutive discharge cycles. All these traces essentially illustrate the discharge dynamics and draw a picture of charges traversing the gap in contact to the connected HV supply. Comparing the voltage waveform in the first and third phase, it is concluded that the observed oscillation period is simply induced by the operation frequency of the switch mode supply, which continued to charge the capacitors during the entire breakdown. The voltage level between both phases is similar, however, the current and also the light emission signals show oscillations in the third, but not in the first phase. These data suggest the following processes to occur in the third phase: After the pronounced avalanches in the main peak of the breakdown, the continuing loading cycles of the switch mode supply efficiently push residual charged electron/ion clouds back and forth between the electrodes with a frequency of $100\ \text{kHz}$. This oscillation essentially *traps* large fractions of the electrons and ions inside the gap. Yet it is not quite clear if the radiation yield is predominantly the consequence of the induced electrical field between

the oscillating, oppositely charged clouds. In this case the deflection may provide sufficient kinetic energy for the electrons to further excite the neutral background gas and thus generate the observed emission. Alternatively, this efficient *charge trapping* may enhance the classical *afterglow* mechanism of pulsed discharges, involving dissociative electron-ion recombination of He_2^+ into a helium ground state atom and an excited He^* with further chemical and radiative decay as discussed in section 3.2.2.1. In this sense, the third region is regarded as an extended *afterglow* following the main peak, caused by the unique combination of the operational mode of the power supply and the spark gap condition. The interesting question on the truly prevailing process in this phase will be addressed during the course of further experiments.

Regardless of the origin of the emission, it becomes evident that the maximum level of the amplitudes in the third phase account for only 10 % of the main peak maximum, however, the *charge trapping* efficiency considerably extends the radiation time, i.e., the area under the curve. Therefore, the *afterglow* essentially contributes more than threefold to the total light output per discharge cycle as compared to the main peak. The concept of *trapped* electrons and ions in this time domain requires further investigation, but it opens up new interesting questions: (i) Can the total light output be enhanced by means of extending the afterglow phase close to a continuous wave lamp? (ii) At what point would it turn into a continuous arc (cf. sections 2.1.3 to 2.1.5)? (iii) What type of dynamics can be initiated by inducing a temporally, spatially and energetically resolved laser plasma in these charged clouds (cf. chapter IV LASER PLASMA)? Future experiments will also cover time and wavelength resolved measurements to investigate specific emission differences between each discharge phase. A new high vacuum to high pressure chamber with several optical ports for VUV, UV-VIS-NIR and IR spectroscopy will be built for improved spectroscopy and better defined experimental conditions. In addition, with a VIS as well as IR high speed camera available, we will provide insight into the time-correlated spatial evolution of the mini spark discharge. Additional simulations with an appropriate software tool will be applied to theoretically substantiate the experimental findings.

3.3.2 Pressure Effects on the Discharge Main Peak

Figure 26 depicts six key parameters of the main peak for the temporally resolved voltage and current waveforms of the miniature spark, recorded under varying pressure conditions with helium as the discharge gas. These plots were adapted from the final DFG report for the project “miniature spark discharge lamps (KE 1816 1-1)” [2].

The upper panel illustrates a voltage (blue - left y-axis) and current (red - right y-axis) trace for the first 4 μs of 1000 averaged discharge events, with the key parameters assigned in red numbers. The lower figures show the corresponding trends of each

parameter with varying pressure. It is stressed that during the displayed 4 μs of the spark event the neutral gas front section moves about roughly 10 % of the electrode distance due to the applied gas flow. In good approximation, the neutral gas can therefore be considered to be at rest during this time. All discussed effects are thus dominated by electrical fields and diffusion but not the gas flow.

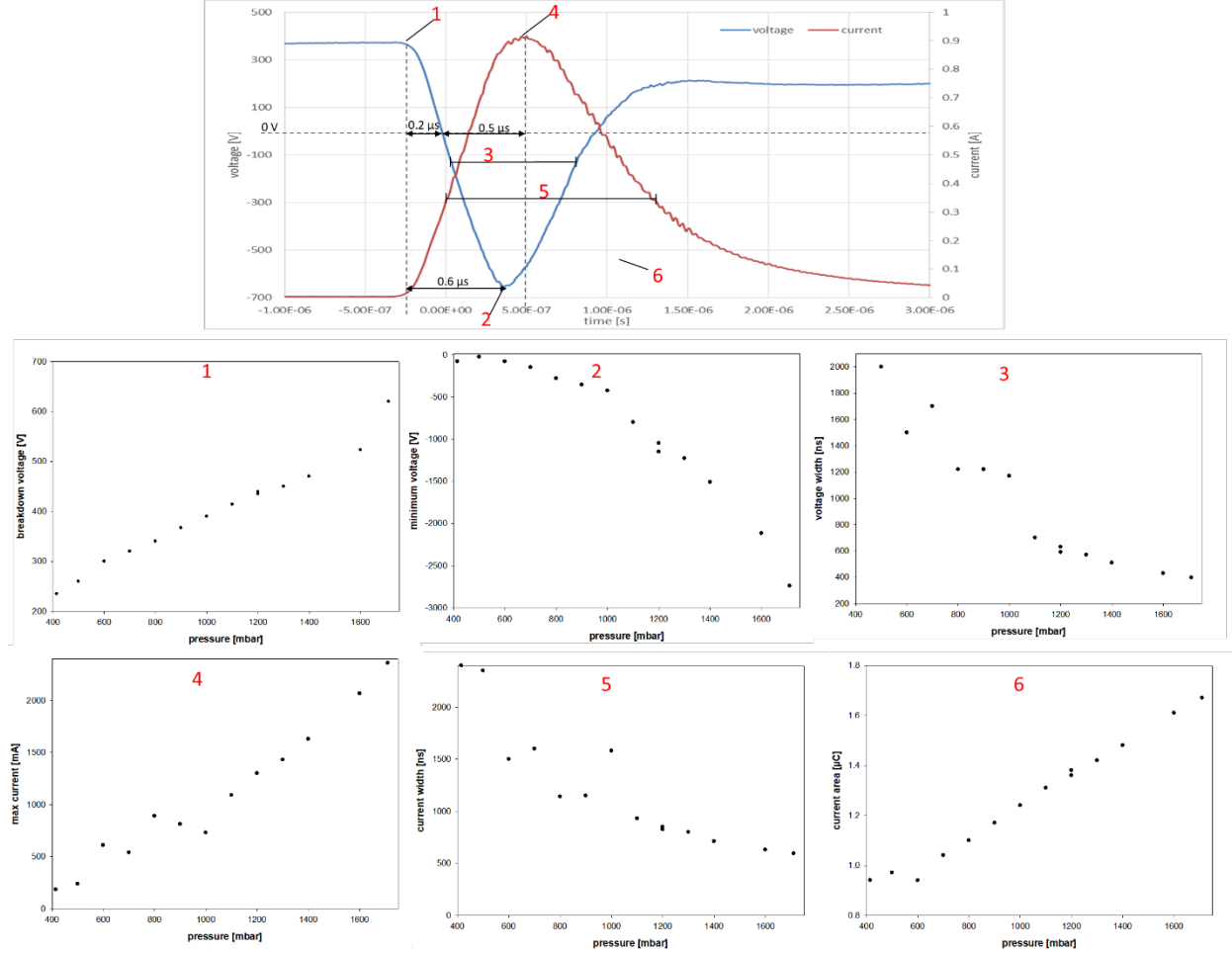


Figure 26 adopted from the final project report (KE 1816 1.1) to the DFG: Illustration on how pressure influences several characteristic features within the time-resolved voltage and current signals of a helium spark discharge.

Dataset #1 depicts the breakdown voltage U_B , an essential quantity to generally characterize a discharge. As shown in the circuit diagram in Figure 12, the positive terminal of the 2 nF capacitor of the HV unit is directly connected to the anode of the discharge gap, whereas the corresponding cathode is connected to ground. After a short trigger pulse, the “electron pump” starts charging the capacitor of the HV unit, causing the increase in the recorded voltage across the gap. This is shown by the blue trace in the top panel of Figure 26 starting at $-1 \cdot 10^{-6}$ s and at around 380 V for the conditions chosen. Note that the entire charging process is not displayed, just the last microsecond before the breakdown event at $-7.5 \cdot 10^{-5}$ s. For inspection of the complete discharge cycle, the reader is referred to the previous section 3.3.1. At point #1 (U_B) the resistance of the discharge gap rapidly decreases due to the discussed avalanche multiplication processes (cf. section

2.1) and finally short-circuits the entire setup as sketched in Figure 12. This results in a steep drop of the voltage measured across the anode and ground. The dependence of this essential event on the gas pressure will be thoroughly treated in the next section 3.3.3.

The second dataset (#2) shows the minimum voltage U_{min} recorded across the gap during a discharge event as a function of the applied pressure. Note that beyond the breakdown point U_B the recorded voltage does not drop to 0 V (indicated by the dashed line) as would be expected for a shorting of a charged capacitor. In contrast, during the spark discharge we observe a large voltage inversion. At the highest pressure of 1700 mbar the breakdown starts at approximately 600 V and drops to a minimum voltage of -3000 V within 0.6 μ s. In contrast, at 500 mbar we find a minimum voltage of merely -25 V. The trend of U_{min} with varying pressure clearly indicates a $(-U_{min}) \sim p^2$ correlation. Responsible for this effect are the dense space charge clouds resulting from the avalanche multiplication process [29]. These clouds travel as “*gaseous electrodes*” through the gap with a considerable momentum, which is partially visualized by the pressure dependency of the voltage and current slopes. At 0 V the driving force between cathode and anode stops and the current vanishes. In Figure 26 (upper diagram) this should occur approximately 0.2 μ s after the breakdown. However, at this point of the discharge event we observe that the electrons liberated from the cathode still produce a current of 0.3 A with a steep increase peaking at 0.7 μ s after the breakdown with nearly 1 A. The fact that the highest rate of liberated cathodic electrons per time occurs at the most negative voltage recorded between anode and ground is compelling evidence for a predominantly space charge driven discharge dynamic. As illustrated in the gap in Figure 12 the electron cloud moves to the anode but the rate of annihilation at the electrode surface and the following high voltage supply cannot compensate for the larger rate of electron liberation and multiplication. As a result, a substantial negative excess charge builds up at the anodic electrode, which eventually causes U_{min} to drop far below 0 V. Thus, the driving force to accelerate liberated cathodic electrons and to sustain the avalanche multiplication processes (cf. section 2.1) has to stem from the residual positively charged cloud slowly moving towards the cathode side. It is then the density and the vicinity of these charged gaseous clouds to the respective electrode determining the further current and voltage progression. With this picture in mind we can at least qualitatively explain the $(-U_{min}) \sim p^2$ correlation of the data set #2. First, a pressure increase at constant reduced field strength results in a larger avalanche efficiency per unit path-length for an electron traveling through the gap. Secondly, a higher pressure reduces the degree of diffusion caused by charge repulsion. Both effects essentially lead to sharper and denser space charge clouds accumulating in front of the electrodes in correlation with increasing pressure. Consequently, a more pronounced *negative* voltage U_{min} is recorded at the anode with elevated gas density. The same arguments apply to the remaining data sets.

The voltage width (#3) is inversely proportional to the pressure and decreases from 2 000 ns to approximately 400 ns between 415 mbar and 1 700 mbar, respectively. This trend is in accordance with the notion of narrower electron clouds in front of the anode at higher gas densities.

The data sets #4 - #6 show current parameters with varying pressure. Note that, the current trace in the top panel of Figure 26 does not simply reflect a discharge in terms of electrons smoothly crossing the gap from the cathode to the anode. Recall that at the same time of the recorded maximum current, the anode is embedded in a dense negative space charge cloud, which essentially repels any approaching electrons back to the cathode. Consequently, the steady increase in the recorded current beyond the 0 V inflection point, i.e., 0.2 μ s after the breakdown, is indicative of a significant positive space charge cloud in the vicinity of the cathode that drives the electron liberation from the metal surface. Therefore, in the same way as the voltage trend displays the discharge dynamics in this phase at the anode, the current slope closely resembles the dynamic of electron liberation from the cathode. With this in mind we can tentatively begin interpreting the dataset #4 in Figure 26. It illustrates the linear change of the maximum current I_{max} by an order of magnitude (approximately 200 to 2 000 mA) in the investigated pressure range. In other words, the highest rate of electrons leaving the cathode per unit time increases by a factor of ten when increasing the pressure from 415 to 1 700 mbar. This effect is attributed to an enhanced secondary amplification driven by the electrical field between the positive space charge cloud and the cathode. As discussed in chapter 2.1.1.2 and expressed in equations (6) and (7), the number of secondary electrons N_{II} depends on the number of energetic particles (ions, photons or metastables) generated per avalanche and an additional factor considering the probability of each particle to impact on the cathode and to release a new electron (*second Townsend coefficient* γ). Since several interrelated mechanisms are operative, each impact on the pressure dependency is rather difficult to exactly deconvolute from this set of data. However, similarly to the considerations on the voltage data, it is reasonable to assume the presence of a denser positive space charge cloud in the vicinity of the cathode at the point of I_{max} with increasing pressure. This does not necessarily alter the reduced field strength (cf. 2.1.1.1), but one electron from the cathode could encounter more high energy collisions with the background gas per unit path length and in total increase the number of energetic particles (ions, photons or metastables). This alone cannot explain an order of magnitude faster electron release, though. The contribution of each energetic species to γ , as expressed in equation (7), is rather tentative at this point. A pressure dependency of the second Townsend coefficient was discussed by Ghosh et al. [112] in terms of increasing the probability of ion-neutralization when approaching the metal surface with subsequent photon emission as the final active species. The results were rather inconclusive and difficult to translate to

the present miniature spark. The impact of metastables is considered to be insignificant, unless the positive space charge cloud is in close proximity to the cathode. Considering only the applied gas flow from the anode towards the cathode, a neutral gas molecule approximately travels $1\ \mu\text{m}$ in $0.1\ \mu\text{s}$. In order to effectively impinge on the cathode, the active area for metastable generation has to be located within the μm range around the electrode surface. This geometrical factor f_m (cf. equation (7)) has to be improved with increasing pressure. Similar arguments apply to photons causing the electron liberation, expressed in the geometrical factor f_p . In order to improve the probability of photons from the gap volume to reach the metal surface, the generation of photons must be in closer proximity and/or the point source must be considerably brighter with increasing pressure. Particularly for such a small cathode as the one used in the miniature spark, little alterations in the photon capture cross section can have huge impacts. To finally deconvolute the contribution of each effect, further experimental investigations, such as time resolved recordings with a high-speed camera, but also profound simulations with elaborate software tools are required.

The last two datasets #5 and #6 show the pressure dependency of the current width and the current area, respectively. Similar to the voltage behavior in #3 we find an inverse relationship for the current width, narrowing it down by a factor of four between 415 and 1700 mbar. The ascending edge of the slope becomes extremely steep, due to the discussed improved secondary electron emission. All previous arguments apply here as well. The current area in dataset #6 shows a linear correlation with pressure between 600 mbar and 1700 mbar, nearly doubling the number of liberated electrons from $5 \cdot 10^{12}$ up to $1 \cdot 10^{13}$. In fact, this trend as well as the total amount coincide with the number of charges to which the capacitor (2nF) of the HV supply was charged right before breakdown, calculated based on the respective breakdown voltage at the considered pressure. At virtually all pressures, the calculated capacitive load constantly accounts for around 65 % of the measured electron release. In the near future, data gathered in all these experiments will be used to obtain more information regarding the discharge dynamics in combination with appropriate simulation tools for mutual validation. Hence, these plots are valuable in terms to partially visualize the evolution and motion of charges through the electrode gap.

3.3.3 Breakdown Voltage

As mentioned in the previous paragraph, the breakdown voltage U_B is an essential discharge parameter and deserves a section on its own. In chapter 2.1.1.2 we thoroughly defined and discussed U_B as the critical voltage at which a self-sustaining discharge sets in at the given conditions (gas composition, pressure, electrode distance, electrode shape,

etc.). In 2.1.1.6, and expressed in equation (8) we then derived its pressure dependency, a semiempirical formula called *Paschen Law*. It has proved to be an extremely useful concept to characterize a discharge setup by comparing the experimental data as shown for the mini spark in Figure 27(a).

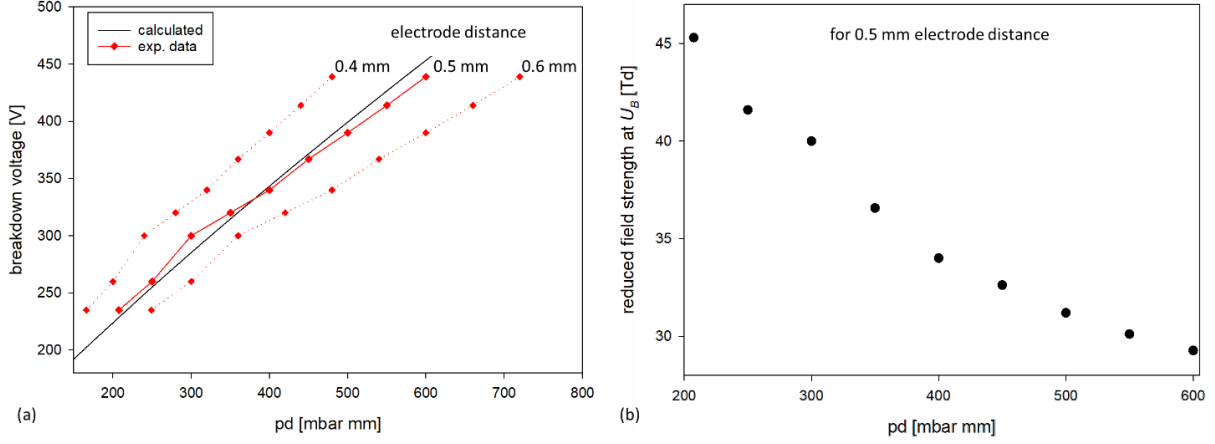


Figure 27: Illustration of breakdown voltage in dependence of the product of pressure p and electrode distance d . (a) Shows the calculated breakdown voltage according to the Paschen Law and the measured breakdown voltage assuming either 0.4, 0.5 or 0.6 mm gap distance, respectively. (b) Determined reduced field strength E_r at the point of breakdown in dependence of pd .

According to the *Paschen Law* the breakdown voltage is plotted against the pd value, the product of pressure and gap distance. Values for the parameters $A = 0.225 \text{ mbar}^{-1} \cdot \text{mm}^{-1}$, $B = 2.55 \text{ V} \cdot \text{mbar}^{-1} \cdot \text{mm}^{-1}$ and $\gamma = 0.01$ were taken from [113]. Interestingly, even newer literature [114] still uses these datasets from 1932. The calculated slope of U_B shows a nearly straight line for the considered pd range. The experimentally obtained breakdown voltages at the different pressures are plotted for gap lengths of 0.4, 0.5 and 0.6 mm. The 0.5 mm dataset compares favorably with the theoretical values and suggests that the initial breakdown phase of the miniature spark discharge is in accordance with the *Paschen Law*. This leads to two essential conclusions: First, the initial phase of the breakdown is not space charge dominated, otherwise considerable deviations are expected, such as in the case for streamers [25]. We can clearly differentiate between the first phase leading to breakdown without space charge and the second phase after breakdown, where space charge builds up and causes the effects described in 3.3.1. Secondly, the gap is not too small to encounter issues caused by insufficient collisions to effectively drive the avalanche processes, as was observed in the field of miniaturizing discharges down to the microscale [43]. Consequently, the mini spark clearly operates in the collision dominated regime on the right branch from the Paschen minimum, where the total number of gas molecules between the two electrodes continuously increases. However, the total number of collisions does not exceed a space charge induced limit, beyond which the breakdown is not simply explained by the mechanism of avalanche multiplication anymore. The same experimental U_B and p pairs of values were additionally plotted with 0.4 and 0.6 mm gaps, respectively. The slopes notably deviate

from theory, which reveals the sensitivity of this system towards the exact adjustment of the electrodes and pinpoint this distance as the most critical parameter.

In accordance with the discussion in section 2.1.1.6, also the reduced field strength E_r at the point of breakdown in dependence of pd was plotted in Figure 27(b). This quantity is a measure for the minimum mean energy an electron must gain between two consecutive collisions with the background gas, in order to initiate a self-sustaining discharge. As expected, with increasing pd value a lower potential energy gradient is required between two collisions to raise the secondary amplification above unity.

Finally, the relevance of a “metastable effect” was investigated by simply reversing the gas flow direction. In case electronically excited neutral species being responsible for the secondary amplification process, a noticeable change of the breakdown voltage is expected. However, no change of U_B was measured. This leads to the conclusion that either ions or, even more likely, high-energy photons are driving the generation of cathodic electrons in this spark configuration.

3.3.4 Wavelength and Time Resolved Emission Profiles for Chemical Kinetics

Principally, the VUV spectroscopic setup allowed for time and wavelength resolved emission profiles to study the kinetics of the prevailing quenching processes as discussed in detail in section 3.2.2.2. Unfortunately, the employed UV-VIS-NIR spectrometer was incapable for such measurements at that time. Consequently, the following is considered as a preliminary and more general discussion on the complex kinetics representative for additional minor gas constituents and their impact on the helium continuum. More recently, a scanning instrument for the 200 - 900 nm range with a PMT detector was purchased, which will significantly contribute to the investigation in this realm in nearer future. The first VUV wavelength resolved emission profiles as a function of time were measured for different species by the former PhD student Mr. Klopotoski and presented at the 2014 ASMS conference in Baltimore, Maryland, USA [62]. An illustrative example is presented in Figure 28 for the helium dimer at 82.0 nm and the atomic emission line of Kr at 123.6 nm. As shown in section 3.2.2.2, an additional trace species to the helium discharge gas significantly reduces the broad He_2^* radiation in favor of intense atomic line emission of the second component.

With 0.4 % krypton added, the He_2^* emission increases within the first 2 μs before the Kr^* radiation evolves and both maxima are approximately separated 2 μs . The present experimental dataset is insufficient to elucidate the underlying mechanism in detail and further comprehensive investigation is required. Nevertheless, some trends become apparent. The direct electronic excitation of Kr atoms through free electrons is negligible.

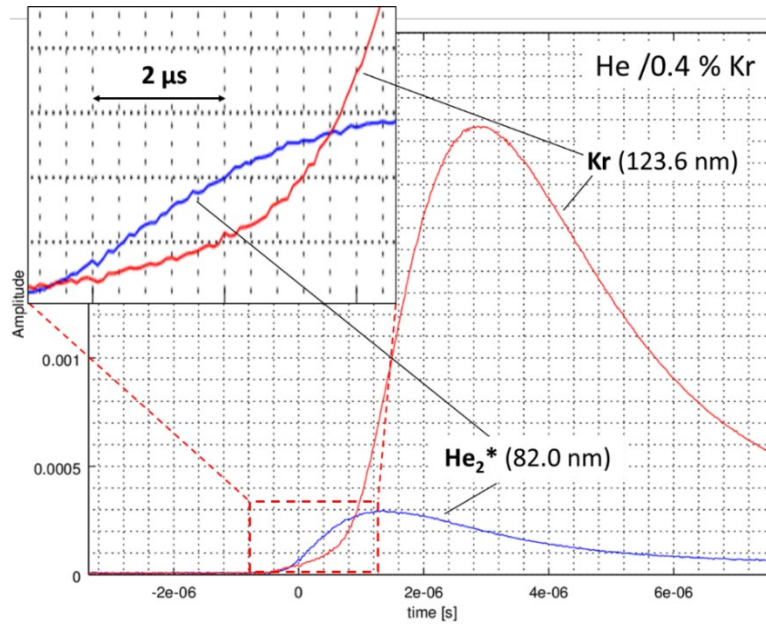


Figure 28 adapted from [62]: Time-resolved emission profiles of the helium dimer at 82 nm and the characteristic krypton line at 123.6 nm. The inset depicts an enlarged view on the initial phase.

According to reaction (1) and (2) the inelastic collision energy of electrons is predominantly imposed on ground state helium atoms to form a multitude of electronically excited states, denoted as He^* and atomic helium ions, respectively. The latter rapidly dimerize to the molecular ion according to reaction (3) and become neutralized through dissociative recombination described by reaction (4), which also generates highly excited He^* species [115, 116]. The various subsequent mechanisms operative to finally form the VUV radiating He_2^* ($A^1\Sigma_u^+$) are discussed in detail in sections 3.2.2.1 and 3.2.2.4. reaction (6) summarizes these steps in a single kinetic equation and reaction (8) expresses the final radiative decay with the familiar helium continuum centered at 82 nm. At this point it is not clear which excited helium species is primarily responsible for the energy transfer to the minor gas constituent. The experimental results evidence an effect on the He_2^* ($A^1\Sigma_u^+$) radiation with the addition of krypton (cf. Figure 14 and Figure 28). Therefore, it could be that once the He_2^* ($A^1\Sigma_u^+$) state is formed, rapid collisional energy transfer according to reaction (9) causes its depopulation.

However, the radiational lifetime of this state was determined as $\tau = 0.55$ ns, corresponding to a fluorescence constant of $k_8 = 1.3 \cdot 10^9 \text{ s}^{-1}$ [65]. This result is rather surprising since all other neutral rare gas dimers show at least two orders of magnitude larger lifetimes. Moreover, our own calculations for the determination of the vibrational state resolved Einstein coefficients (cf. section 3.2.2.3) show considerable variations between $1 \cdot 10^6 \text{ s}^{-1}$ and $4 \cdot 10^8 \text{ s}^{-1}$ for the lowest ($v = 0$) and the highest ($v = 16$) vibrational level, respectively. This finding suggests that the lifetime strongly depends on the vibrational state distribution and has to be considered. The single value for the fast radiative decay from literature implies that a parallel reaction with krypton directly

depopulating the He_2^* according to reaction (9) is less probable. Consequently, a precursor feeding the He_2^* ($A\ ^1\Sigma_u^+$) state is required to react with krypton. In reaction (7) this is illustrated for the atomic metastable state He^* (2^1S). However, the competing association in reaction (6) should be much faster under the present experimental conditions. This was evaluated by Pouvesle et al. for the 2^3S excited state and should apply for the 2^1S as well [108]. Alternative precursors are the different excited molecular states as shown in Figure 15 and discussed in section 3.2.2.1 and naturally the ionic helium species as expressed in reaction (5). Currently, the insufficient dataset renders further elucidation of the underlying depletion mechanism highly speculative. Nevertheless, due to the low ionization energy of krypton ($IE = 14\text{ eV}$) [41] as compared to the lowest excited helium state of 18 eV (cf. Figure 15), we can expect that any of the feasible helium species exclusively lead to the formation of Kr^+ via reaction (7) and (9). These steps are followed by a termolecular recombination via reaction (10), stabilized either through a second electron or a helium atom. The pathway via a heteronuclear ion HeKr^+ with subsequent dissociative recombination into a Kr^* state is deemed negligible due to its rather low binding energy of 23 meV [115]. In contrast, for other mixed rare gas ions, such as HeNe^+ with 700 meV binding energy, this route does generally contribute to the electronic excitation of the heavier species present in a binary composition [115].



Finally, we conclude that the multiple step mechanism via ionization of krypton through excited/ionized helium species with subsequent electron-ion recombination to form Kr^* readily explains the observed time delay between the two radiating channels in Figure 28. The ionic route should in fact be observed in time resolved UV-VIS-NIR spectra as well, since between reaction (10) and (11) a fluorescing cascade in the visible is very likely. Furthermore, a considerable dependence on the electron energy distribution is expected for reaction (10) [89], which should essentially impact on the temporal responses for the different discharge phases shown in Figure 25. A corresponding experimental setup to further address these open questions is currently in preparation.

3.3.5 Effect on the Current-Voltage Characteristics upon Oxygen Addition

Trace constituents added to the helium discharge do not only alter the radiative output (cf. section 3.2.2.2), but also significantly impact on the discharge dynamics with regard to the temporal current and voltage evolution. As discussed in the introduction of the *Townsend Discharge*, additional species with lower ionization energies significantly enhance the primary electron avalanche process and result in an effectively lowered breakdown voltage (cf. 2.1.1.4). On the other hand, the amount of freely available electrons as well as their high mobility can be specifically reduced through an additional component present. In particular large molecules with a number of vibrational/rotational degrees of freedom and electronegative species significantly alter the electron mean kinetic energy, the fundamental property of any discharge and plasma dynamics (cf. 2.1.1.3 and 2.1.1.5). A prominent and technically relevant example for the latter is the application of SF_6 as a dielectric to prevent unwanted avalanche processes in gas insulated high voltage components [117].

In his master thesis work and within the course of the DFG project [2], Sebastian Winkelmann recorded time resolved current and voltage progressions with varying discharge gas compositions [7]. The following results were obtained with pure helium and a mixture of helium with approximately 40 ppmV oxygen present, respectively. In both cases the pressure was maintained at 1080 mbar. Figure 29 depicts the corresponding traces for the *main peak* of the discharge cycles (cf. Figure 25) during the first five microseconds. The current and the voltage trends for pure helium essentially follow the ones presented in section 3.3.2. At the breakdown condition of 370 V the current steeply increases within 0.7 μs to 1 A and exponentially decays for 3.5 μs . The voltage shows the discussed inversion across the 0 V line to - 600 V and recovers within 1 μs to a plateau of 200 V. In stark contrast, the gas mixture revealed considerable different behavior of the discharge dynamics with regard to several aspects. First of all, the breakdown voltage increased by 55 V to 425 V. This is expected, considering the increased kinetic energy loss

in ro-vibrational modes of O_2 and the feasible electron attachment to form O_2^- and O^- (cf. 2.1.1.3 to 2.1.1.5). The first process effectively reduces the electron mean kinetic energy and the latter essentially reduces the total number of free electrons. However, the alteration due to merely 40 ppmV additional oxygen remains surprising and requires further detailed investigation, for example through advanced plasma simulations.

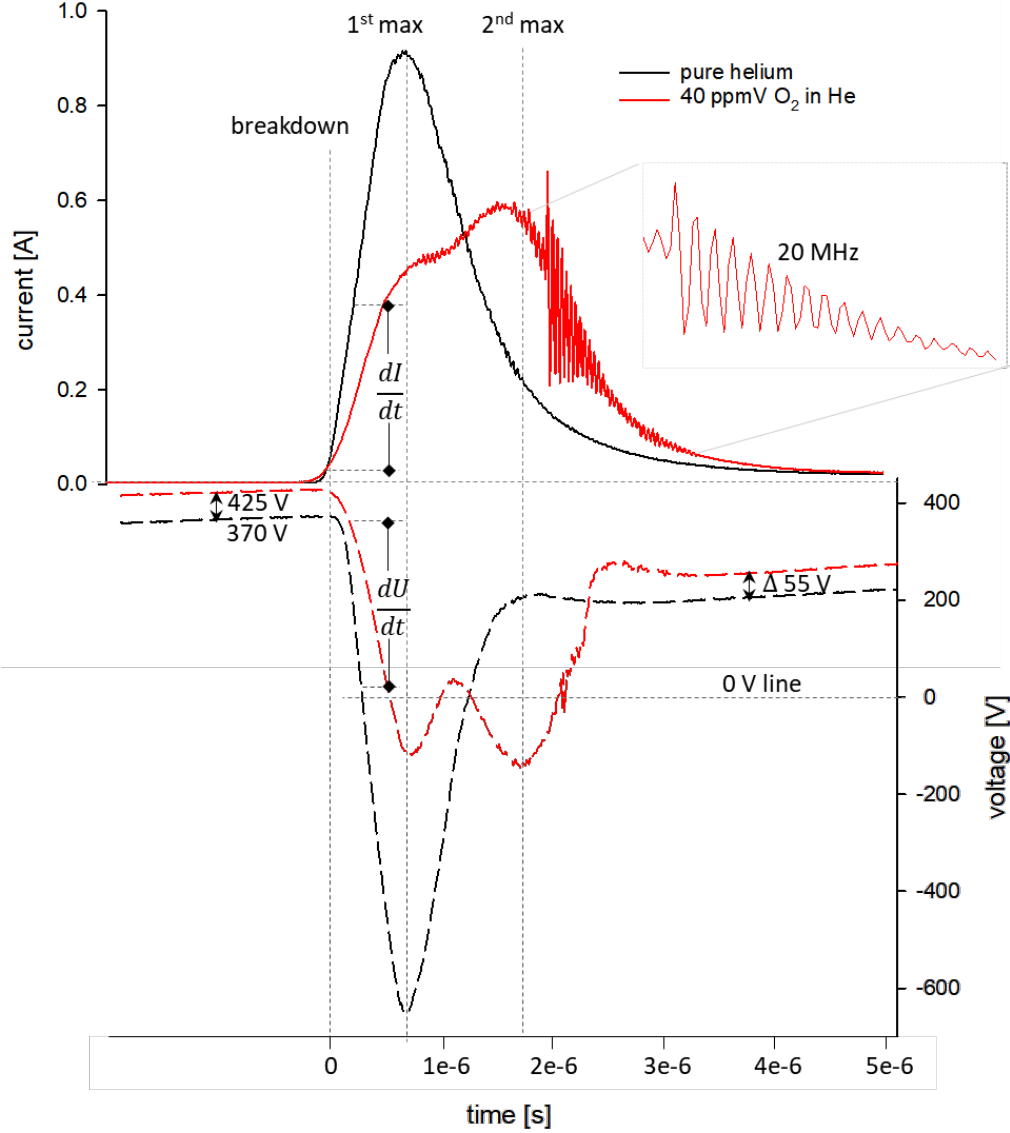


Figure 29 (data collected by Mr. Winkelmann [7]): Illustration of the effect of 40 ppmV oxygen addition to a helium spark discharge at 1 080 mbar on the temporally resolved current and voltage signals of a single breakdown event.

Following the point of breakdown, we also observe notable differences between the two gas compositions with regard to the initial linear slopes of the current increase and the respective voltage drop. The corresponding rates for the pure helium and the helium/oxygen mixture were determined as $\frac{dI}{dt} = 1.6 \cdot 10^6 \text{ A} \cdot \text{s}^{-1}$ and $6.8 \cdot 10^5 \text{ A} \cdot \text{s}^{-1}$, and for the voltage as $\frac{dU}{dt} = -2 \cdot 10^9 \text{ V} \cdot \text{s}^{-1}$ and $-1 \cdot 10^9 \text{ V} \cdot \text{s}^{-1}$, respectively. Hence, both rates are reduced by a factor of two upon oxygen addition. In other words, 40 ppmV O₂ slow down

the avalanche process by approximately 50 %, relative to the pure helium discharge condition. Subsequent to the steep linear current increase and voltage drop we find the most striking difference between the two gas compositions. In the presence of oxygen, a double peak structure forms with two distinct maxima, in contrast to just one maximum in case of pure helium. It appears that the first maxima are all aligned at 0.7 μs after the breakdown. In case of the admixture, the heights are significantly reduced and we obtain 0.4 A instead of 1 A and -100 V instead of -600 V for the current and voltage maxima, respectively. The second maximum for the He/O₂ composition forms 1.7 μs after the breakdown. The voltage slope in the double structure is reasonably resolved, whereas for the current it is far less pronounced. The underlying processes causing these observations is still up to speculation. However, we can state that it reflects the altered mobility of the negative charges and that these measurements provide further valuable information on the dynamics of the moving electron and ion clouds through the gap of the mini spark.

After the second maximum an exponential decay follows, however, in case of the admixture with a strong oscillation of approximately 20 MHz. Note that the HV supply induced oscillation as discussed in section 3.3.1 has a frequency of 100 kHz and is superimposed on the afterglow (cf. Figure 25) starting 10 μs after the breakdown, which is not depicted in Figure 29. Therefore, this “instability” in the main peak cannot be caused by the HV supply. Another interesting observation in this experiment was the voltage level difference of 55 V between the pure helium and the He/O₂ condition at the transition to the afterglow phase. This value exactly matches the difference in the breakdown voltage. Again, the reasons for this behavior are not completely understood yet and further detailed investigations are required to fully rationalize the underlying complex dynamics.

3.4 Plasma Parameters

The number density n_e and the temperature T_e (energy distribution) of electrons basically determine the overall plasma properties. Closely related are the Debye length λ_D

$$\lambda_D = \sqrt{\frac{\epsilon_0 \cdot k_B \cdot T_e}{n_e \cdot e^2}} \quad (13)$$

and the plasma frequency f_p ,

$$f_p = 9000 \cdot \sqrt{n_e} \quad (14)$$

two essential parameters generally used to characterize a plasma [118]. The Debye length is a measure for the mean penetration depth of the electrical field into the gas volume induced by an individual ion. It is proportional to T_e , inversely proportional to n_e and depends on three constants – the vacuum permittivity ϵ_0 , the Boltzmann constant k_B and

the elemental charge e . Higher electron densities reduce λ_D due to enhanced shielding of the individual ions, whereas higher electron temperatures increase the Debye length since the average electron distance in proximity to the positive charge increases as well. f_p describes the natural frequency of the plasma electrons to oscillate around an equilibrium position upon perturbation. This parameter only depends on the electron density as a variable. The constants in this equation sum to the factor 9000 when n_e is expressed in units of cm^{-3} .

For the pulsed mini spark as a transient plasma these characteristic measures largely change along a discharge cycle. So far, we did not have the means of determining the temporally resolved electron temperature nor the exact electron density. Nevertheless, the integral of the current curves $\int I(t)$ in section 3.3.2 provide an idea of the absolute number of electrons N_e traversing the gap during the main peak (cf. Figure 25). We can compare this with the total charge load of the HV capacitor, calculated by simply multiplying the respective breakdown voltage with the capacitance (2 nF) and the number of elementary charges per coulomb. Figure 30 depicts both measures in dependence of the gas pressure. The capacitor load exactly follows the breakdown voltage/pressure curve (cf. Figure 26 #1) and we obtain a total of $3 \cdot 10^{12}$ up to $1 \cdot 10^{13}$ charges in the considered range. In comparison, the electron numbers derived from the integrated current/time curves of the main peak also show linear behavior that differs by a constant offset of $2 \cdot 10^{12}$ electrons and a slightly higher slope. At this point it seems rather speculative to simply relate this trend to the avalanche efficiency. However, it is indicative for a well-established mechanism that clearly determines the heights and length of the current peak in dependence of the total capacitor load and gas pressure.

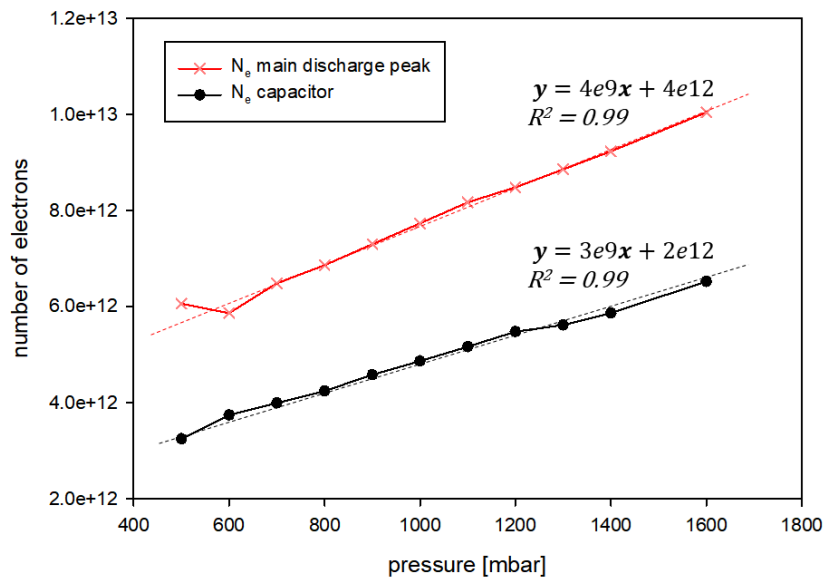


Figure 30 (data collected by Mr. Winkelmann [7]): Absolute numbers of electrons from helium spark discharges in dependence of the employed pressure. (red) Measured at the anode and (black) determined for each corresponding capacitor load.

From these numbers we can tentatively get a rough idea on maximum electron densities, presuming all electrons being freely located between the electrodes within a cylindrical gap volume of 1 mm electrode diameter and 0.5 mm gap length. This approach results in maximum densities of $n_e \approx 1 \cdot 10^{16}$ electrons per cm^{-3} , translating to a maximum plasma frequency in the terahertz range. Assuming an average electron energy of roughly 5 eV ($5.8 \cdot 10^4$ K) we obtain Debye lengths of $\lambda_D \approx 1 \cdot 10^{-7}$ m, which is in the range of the typical mean free path of neutral molecules at standard conditions. As mentioned, these results can only be regarded as upper limits, since we do not have enough experimental data yet to draw final conclusions. Prospectively, appropriate simulation tools will be employed to visualize the transient character of the spark discharge with rapidly changing electron energies and also to include the anisotropy of charge distribution along the gap.

3.5 Electrode Corrosion

Electrode corrosion is a common observation in plasma setups applying metal electrodes. After several month of intense operation, the mini spark assembly used with the VUV spectrometer (cf. Figure 8(b)) was removed and disassembled. The electrodes were closely inspected with a microscope camera and the results are shown in Figure 31.

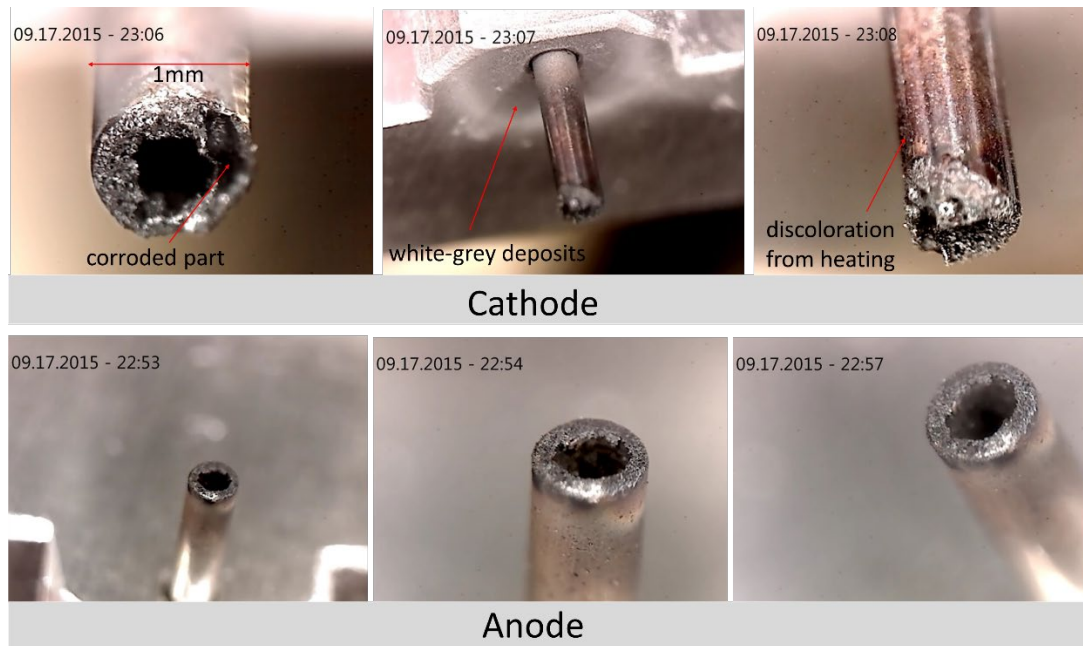


Figure 31: Microscopic images of the cathodic and anodic mini-spark electrodes reveal corrosion damage after several months of intensive use.

The abrasion marks on the cathode are clearly apparent. Particularly the inhomogeneous pitting and the discoloration reflect the intense bombardment of ions on the surface and the buildup of considerable heat on the first millimeters of the electrode. In addition, white-grey colored deposits were found on the cathode holder, which most probably

originate from the sputtered metal surface. Note that for all experiments described in section 3, the discharge gas entered the gap through the anode and was actively pumped through the cathode. This readily explains the rather located depositions on the mounting around the cathode feedthrough. The notable pitting is indicative of plasma sheaths formation around the cathode with strong electrical field strength during spark operation. The cathode fall causes positive ions to be accelerated towards the grounded electrode. As a rule of thumb, the sheath distance from the cathode is on the order of the Debye length λ_D , thus approximately in the μm range when applying the rough calculation from section 3.4. With these findings, it seems possible that ion bombardment as a secondary amplification process (cf. section 2.1.1.2) cannot be neglected and may play an important role at least during the main peak of the discharge cycle, when considerable space charge clouds are being formed (cf. section 3.3.1).

In contrast to the cathode, the anode surface seems nearly unaffected by the impinging electrons. The small, black and uniform ring around the aperture is caused by the grinding of the originally sharp medical cannula.

4 Metastable Measurements

The results described in this chapter were also presented at the 2013 ASMS conference in Minneapolis, Minnesota, USA in 2013 [119].

In chapter 3.2.2 the versatility and flexibility of accessible VUV radiation recorded at atmospheric pressure was demonstrated. Depending on the respective conditions the high energy output of the mini spark is adjustable to a certain degree and applicable on a small and bright spot. Besides light emission, the question on the impact of metastables as high energy particles under such conditions remained. As discussed in chapters 3.2.2.1 to 3.2.2.3 and 3.3.4 they play a pivotal role in the overall discharge chemistry, however, at atmospheric pressure the generation as well as de-excitation of metastables is rapid.

In the literature several methods for measuring metastable species are described, most of them are based on spectroscopic approaches with selective laser excitation followed by ionization or an unique relaxation pathway indicative of the initial state [120-122]. In the DFG project [2] we proposed to assess these energetic states with a mass spectrometer through appearance energy measurements similar to the work of Long et al. [123]. They used a double-electron-beam technique with the first electron beam generating helium metastables and the second for elevating those into an ionized state with subsequent mass detection. In our setup this first beam was replaced by the plasma source. The principal idea behind this method is rather straight forward. Metastables require less energetic electrons for ionization than the respective ground state species, which allows to

distinguish the two. For helium, the ionization energy from the ground state is 24.6 eV whereas, e.g., from the lowest $\text{He}(^3S_1)$ state at 19.8 eV only 4.8 eV are required (cf. Figure 33(b)). Differentiating the manifold of electronic excited states should be possible with this technique. The molecular species $\text{He}_2^+ A\ ^1\Sigma_u^+$ and $a\ ^3\Sigma_u^+$ in their respective vibrational ground states differ by 0.4 eV (cf. Figure 15). With a suitable ionization source, these should be separated in an electron energy scan. However, today, most commercially available mass spectrometers are not equipped with high resolution EI sources.

Nevertheless, to establish appropriate experimental conditions, we opted for a molecular beam quadrupole mass spectrometer from a known manufacturer in the plasma community (HPR-60, Hiden Analytical Ltd, Warrington, UK). This instrument is equipped with an atmospheric pressure inlet and a suitable vacuum system to handle high loads of typical plasma gases. Moreover, it allows to adjust the electron energy between 0 and 300 eV with a resolution sufficient to differentiate at least between ions generated from the ground and a metastable state, respectively. In order to best possibly resemble the discharge conditions as used for the spectroscopic part, setup I was designed as shown in Figure 32.

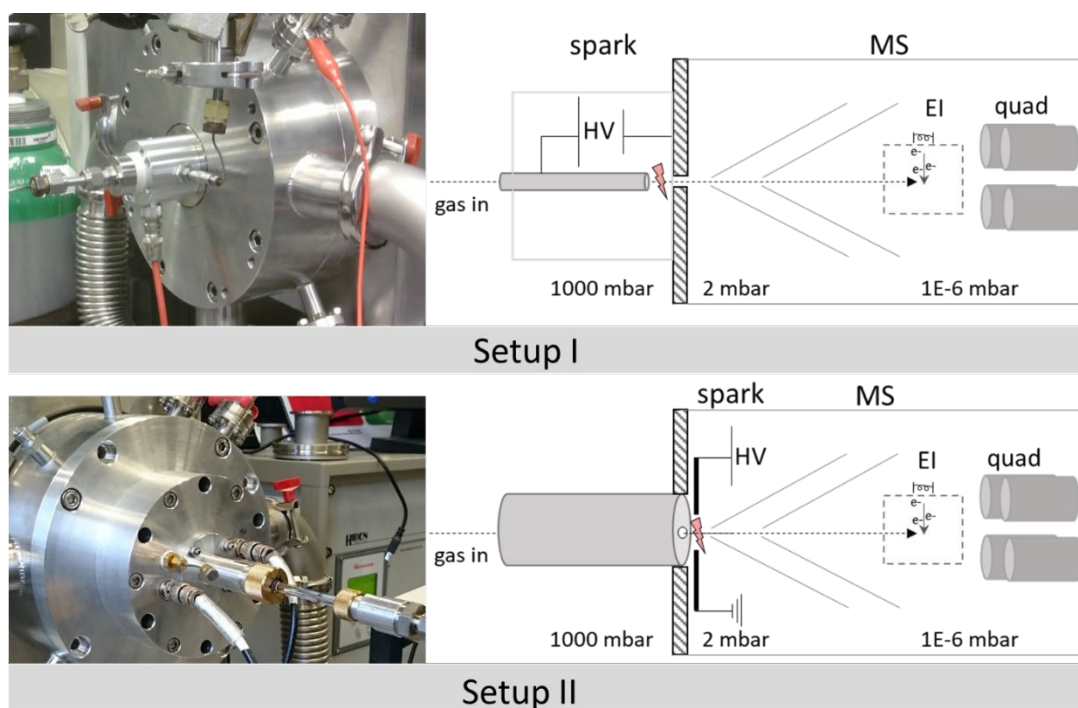


Figure 32: Photographs and corresponding sketches of two adapted spark discharge sources designed to interface with a mass spectrometer for metastable species measurements. Setup I (designed by the author) operates at atmospheric pressure (1 000 mbar), while Setup II positions the discharge within the first differential pumping stage of the mass spectrometer (designed by Mr. Kłopotowski).

The spark gap length as well as the anodic electrode remained the same. For the grounded cathode the original stainless-steel orifice plate of the mass spectrometer was used to maintain the plasma close to the entrance region. The entire spark design was

encapsulated (for more details the reader is referred to section 5.2) and pumped through the 0.2 mm MS aperture. The gas flow was adjusted in the range of 300 to 500 sccm to adjust the discharge gap pressure between 600 and 1000 mbar. In order to reduce the signal noise on the traces m/z 4 and 8 for the atomic He^+ and the dimer He_2^+ , respectively, the massive native ion load from the plasma was prevented from entering the quadrupole by applying repulsive potential gradients between the upstream skimmers. Furthermore, single ion counting with up to 5 s dwell time for each electron energy step and continuous raw data accumulation over several hours were used to improve the sensitivity.

Despite several attempts using various experimental conditions, setup I failed to prove the existence of plasma generated metastables. Changing the plasma gas to argon with metastable states principally amenable to this detection method did not provide the desired results either [119]. One major concern were residual gas impurities in the plasma region, since the lowest attainable pressure was only around $1 \cdot 10^{-2}$ mbar at this point. This was further proven by the respective mass spectra. Therefore, it was reasonable to assume a rather efficient metastable quenching process in setup I upstream of the EI source. However, at that time we did not have the means to provide a more elaborate vacuum system for evacuating the spark volume. Hence, setup II was designed to reduce secondary reactions of metastables simply by lowering the total collision number with less gas density and less dwell time in high pressure regions. This required a redesign of the first pressure reduction stage as shown in Figure 32. Essentially, instead of an aperture geometry separating the high pressure from the first differential pressure stage, a glass capillary was used. Close to the capillary exit an electrode assembly was mounted to maintain a spark discharge in the gas expansion region. Note that this spark arrangement does not resemble the conditions used for the spectroscopic investigations; in particular the discharge pressure is more than two orders of magnitude lower, which certainly affects the physical and chemical properties. However, the primary reason for using setup II was proving the principal feasibility of this mass spectrometric approach to observe metastables. Similar to the first setup, repelling voltages were applied to prevent plasma ions from entering the analyzer. Additionally, the signal recording with ion counting and data accumulation was used. With all these settings we were able to record electron energy scans on m/z 4 with the operating helium plasma as shown in Figure 33(a). At first instance, the slope appeared to reveal the expected and hoped appearance energy of a helium metastable at 6.5 eV, with an offset of 1.7 eV (cf. Figure 33(b)). However, with the plasma turned off the same curve was obtained. Many attempts were made to locate this erroneous finding. The most reasonable explanation is that at -6.5 V applied to the EI source, electrons begin to drift upstream towards the inlet skimmers, where they are accelerated to over 200 eV - due to the required repelling voltages - and then ionize neutral helium.

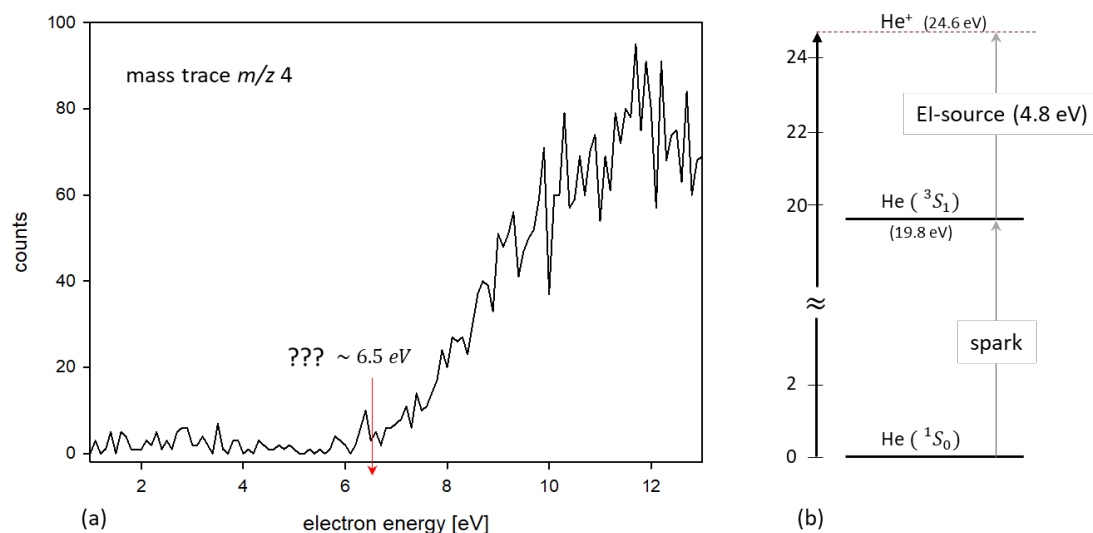


Figure 33: (a) The measured mass trace at m/z 4 as a function of electron energy was initially thought to indicate the presence of metastable species generated in the spark discharge (cf. setup II, Figure 32). However, further investigation revealed it to be an artifact of the instrumental setup itself. (b) Scheme of the mass spectrometric approach for the detection of metastable species.

In conclusion, to date we were not able to detect metastable species with the applied mass spectrometric method. A major issue are residual gas impurities in the plasma region of the spark assemblies used. Continuing work with this approach require a substantial modification of the MS inlet, which is planned. Alternatively, a spectroscopic experimental setup with newly purchased optical parametric oscillators (200 and 4500 nm) may be used for qualitative and quantitative determination of spark plasma generated metastables. Work in this realm is in progress.

5 Applications and Designs

5.1 Sparks in Liquid Nitrogen for Proton Capture

The motivation for this initial project was to investigate the extend of proton solvation in liquid nitrogen. Generally, a proton is thermodynamically stabilized between nitrogen molecules. In gas phase the cluster formation $\text{N}_2\text{-H}^+\text{-N}_2$ from a protonated and a neutral nitrogen molecule is exothermic by approximately $60 \text{ kJ}\cdot\text{mol}^{-1}$ and exergonic by $35 \text{ kJ}\cdot\text{mol}^{-1}$ [124]. Both, the protonated monomer and dimer have drawn much attention in the last decades, in particular as species significantly contributing to the total nitrogen budget in interstellar regions [125]. Many efforts were undertaken experimentally as well as theoretically to describe the electronic structure and spectroscopic features [126] in this realm. Our interest in these ionic molecules arose from their unique properties for proton transfer ionization in analytical mass spectrometry, as discussed in detail in section 4.2.4 (III HELICAL RESONATOR PLASMA). Figure 34 depicts the dimer, a linear and symmetric molecule with the proton equally centered between the two nitrogen

ligands ($D_{\infty h}$ symmetry). Using our own DFT calculations with the RB3LYP method and a 6-31++G(d,p) basis set we obtained equilibrium spacings of 1.28 Å and 1.10 Å for the N-H and N-N bonds, respectively. These values agree within 1 % with data reported by Yu et al. [125]. However, not much is known about the behavior of protons in liquefied nitrogen. Works of Doake et al. [127] and Henson et al. [128] investigated the mobility of positive charges through liquid nitrogen. For ion generation they used a radioactive source and corona discharge, respectively, directly immersed in liquid N_2 . The detected species were not further specified but are assumed to be of $(N_2)_x^+$ type.

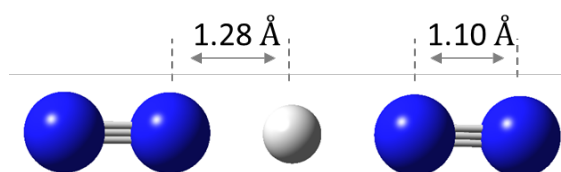


Figure 34: Geometry of the proton bound nitrogen dimer, calculated via DFT with the RB3LYP method and a 6-31++G(d,p) basis set.

For his master thesis in our group Dr. Robin Hillen investigated the feasibility generating protonated nitrogen in liquid phase [6] using the spark assembly and alternatively a corona discharge. He developed setups to operate the plasmas in gas bubbles immersed in liquid nitrogen. For charge detection Mr. Hillen used a potentiostat and a mass spectrometric adaption. Many attempts and optimization steps were undertaken but unfortunately within his work Mr. Hillen could not prove the existence of ions in liquid N_2 generated by the respective plasmas. The uptake of initial gas phase ions through the boundary into the liquid nitrogen is a critical step, which is not well understood yet. Furthermore, the ion detection methods, in particular in combination with the mass spectrometer, were more difficult in the detailed realization than expected. So far, this topic has not been pursued any further, but remains of fundamental interest.

5.2 GC-Orbitrap with Spark Discharge Ionization

In a major project between 2012 and 2015 the author worked with Prof. Dr. Makarov (inventor of the Orbitrap MS Technology) from Thermo Fisher Scientific on the development of a GC-Photoionization source interfacing to the Orbitrap MS series. Initially, two different concepts were developed, one based on the miniature spark discharge and one based on a helical resonator plasma. Prototypes for both concepts were built and tested, of which Thermo Fisher Scientific decided to proceed with the latter. The course of this design process to market maturity and its launch with MasCom Technologies GmbH in 2016 will be presented in detail in chapter III HELICAL RESONATOR PLASMA section 3. Though the spark source has not been further pursued

to result in a final analytical application, the concept, advantages and drawbacks will be briefly presented in the following. The prototype shown in Figure 35(a)-(c) was designed to combine mass spectrometric with spectroscopic information to detect compounds from a gas chromatographic run.

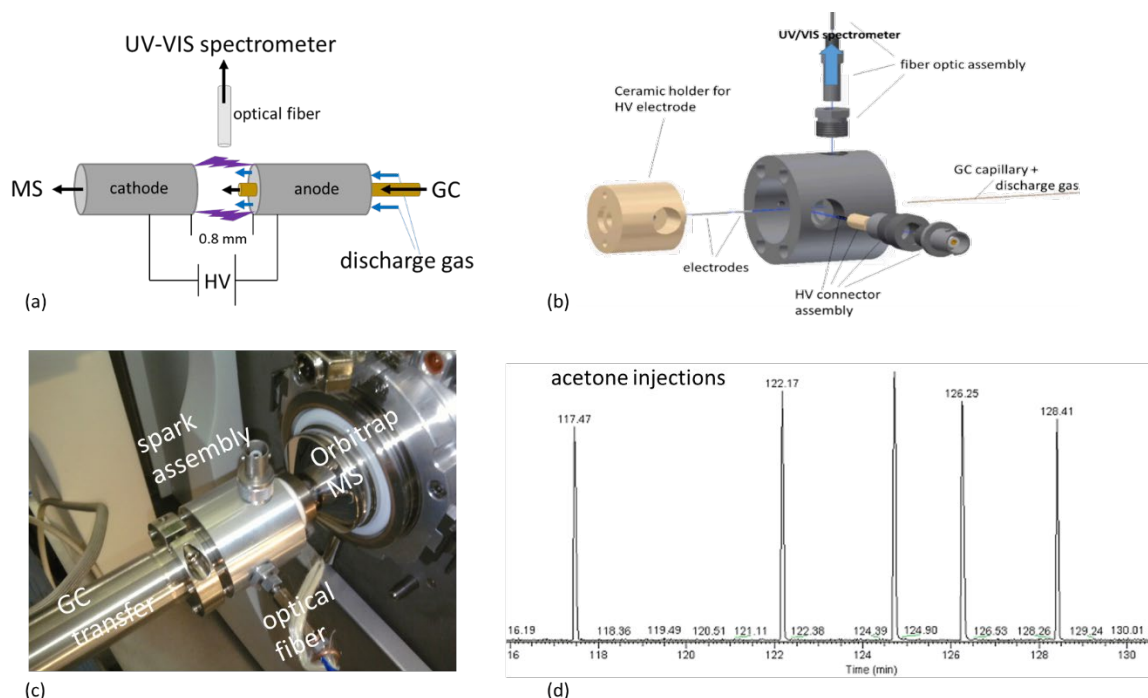


Figure 35: A spark discharge source interfaced to an Exactive Orbitrap mass spectrometer for the simultaneous measurement of GC separated compounds via mass spectrometry and characteristic fluorescence signatures. (a) Schematic of the setup, (b) exploded view of the spark source design, (c) image of the final lab setup and (d) chromatogram of several subsequent acetone injections recorded with the MS.

Essentially, an electrode configuration with 0.8 mm gap distance and a GC column fed through the anode with 0.1 mm protruding into the gap was enclosed in a vacuum tight and high voltage secured housing (cf. Figure 35(a)). Common GC gas flows between 1.5 sccm and 3.0 sccm of helium were used, sheathed by approximately 1 400 sccm of argon as the primary discharge gas. The total cathodic effluent was directly fed into the transfer capillary of the Orbitrap MS. An optical fiber arranged perpendicularly with respect to the spark gap transmitted the plasma generated radiation to a UV-VIS-NIR CCD spectrometer.

This ionization source concept features the detection of GC separated compounds by characteristic light emission in addition to the mass spectrometric information. The open plasma environment eluting compounds are exposed to provides several energy transfer processes for electronic excitation and ionization, such as the interaction with primary plasma ions, metastables and fast electrons. However, this concept is accompanied by many unknowns, particularly the extent of contribution of each process is hard to predict and control. Presently, no viable model exists concerning the spatial and temporal electron density and energy distribution during the transient miniature spark in the

presented electrode configuration. In fact, we do not know if the electrons follow the electrical field as indicated by the purple plasma region in Figure 35(a), which suggests a donut shaped spatial distribution from the cathode to the anode. In this case, assuming negligible diffusion from the GC outflow, eluting compounds are more likely “sheathed” by the plasma and the excitation contribution through direct interaction with energetic electrons should be rather insignificant. However, the time resolved measurements of voltage, current and emission characteristics of single discharge cycles as presented in section 3.3 showed strong space charge effects, inducing transient electrical fields that clearly diverge from the indicated and simplified field lines.

In preliminary experiments, results obtained after consecutive acetone headspace injections demonstrated the principle of the ionization and ion transfer capabilities of the spark prototype, as depicted by the chromatogram in Figure 35(d). The corresponding mass spectra mainly showed the protonated monomer and dimer. Characteristic radiation in the UV-VIS region, induced by the eluting compound, were not detected in these initial investigations. The mini spark setup used for the fundamental characterization in the previous chapters showed carbon emission in the presence of hydrocarbon impurities from the oil sealed rough pump, in particular in the VUV at 193, 166 and 156 nm (cf. Figure 17). However, corresponding radiation in the UV-VIS-NIR range has not been observed with those unspecified impurities.

This is the status quo of this spark discharge ionization prototype. It allows pursuing many interesting experiments with respect to optimization steps leading to real analytical applicability, and also in terms of fundamental issues: Why do we observe atomic carbon emission and at the same time intact protonated hydrocarbon molecules? What are the underlying mechanisms? Using a fused silica fiber and an appropriate spectroscopic setup, can, e.g., the 193 nm radiation of C* be used as an analytical tracer for eluting hydrocarbons? To answer such questions and optimize this open plasma approach a comprehensive survey is still required. The plasma conditions have to be further optimized, feasible characteristic emission of certain compounds and functional groups have to be thoroughly investigated, an active heating system has to be implemented for real GC compatibility, the impact on mass spectra with respect to ion transformation processes (oxidation, fragmentation) needs to be evaluated, the MS and spectroscopic data system require synchronization and implementation into one software - just to name a few critical issues. Therefore, Thermo Fisher Scientific decided against this concept and favored the helical resonator approach (cf. section 3.2 in chapter III).

5.3 Aerosol Spark Discharge Ionization

In 2016 the Swiss Tofwerk AG requested an alternative desorption and ionization concept for an aerosol chemical speciation monitor. In general, this instrument samples airborne particles and analyses their chemical composition [129]. The common system operates with an aerodynamic lens selectively guiding aerosols through a differentially pumped vacuum chamber onto a collector plate. Following a certain sampling time, the plate is rapidly heated and the vaporized material is exposed to classical electron ionization. Generated ions are subsequently guided to a mass analyzer. The proposal was to replace the original sampling/vaporization and ionization stage with a spark discharge unit. In principal, accelerated electrons or ions impinging on a surface are capable of ablating and ionizing deposited material in-situ. As shown in Figure 36, the concept envisaged a two-step procedure: (i) aerosol sampling on a stainless-steel filter and (ii) aerosol vaporization and ionization in a spark driven process. The cylindrical filter is a standard consumable from Swagelok® and available with different pore sizes. This allows to swiftly replace the filter material and additionally select the particle size of interest. A 1/32" stainless-steel tubing is inserted into the filter and held in place by a dielectric isolator, which covers most of the inner surface such that particles are deposited and ablated only within a small spot. On the other end a T-piece connects to the air inflow and the inlet of an atmospheric pressure MS interface. In this configuration aerosols are sampled on the filter using a vacuum pump, connected via a three-way valve. Following a defined sampling time, the gas flow is reversed with an appropriate discharge gas (e.g., argon). The valves to the sample line and MS are set to a closed and open position, respectively. Sparking between the sample area and the end of the stainless-steel tubing is then induced by the connected high voltage power supply (cf. Figure 6 (b)).

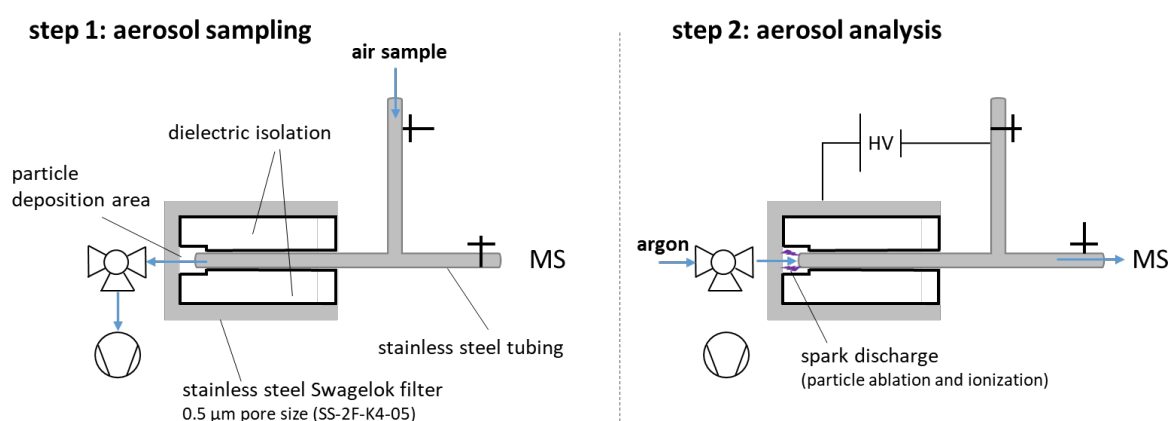


Figure 36: Concept diagram for an aerosol analysis system combining aerosol sampling, ablation/ionization with a modified spark discharge source, and subsequent mass spectrometric analysis.

A related spectroscopic approach was presented by Diwakar et al. in 2012 [130]. They used a corona discharge as an electrostatic aerosol collector with a subsequent spark initiated *hot arc* plasma for vaporization and electronic excitation. Characteristic

fluorescence allowed to identify and quantify certain elements the aerosol was composed of.

In contrast, the concept presented here applies a *cold* plasma for vaporization and ionization. A provisional modification of the GC-spark source described in section 5.2 with a respective filter setup attached to a time-of-flight mass spectrometer provided initial promising results with NaCl vapor and the subsequent detection of sodium ions. Dr. Bräkling and Dr. Rieger obtained these results during their undergraduate research internship. However, a conclusive proof of concept is still pending, since the Tofwerk AG did not further pursue this initiative.

5.4 Capillary Electrokinetic Separation

In 2009 we reported on adverse effects of ion chemistry in modern API-MS instruments [20] and have been investigating techniques to reduce those ever since. Considering a total collision rate of $1 \cdot 10^9$ per second, the challenge is to minimize the number of *reactive* collisions following the ionization step within a generally reactive neutral matrix. Apart from water and abundant residual neutral analyte, most API sources with a plasma induced ionization step (corona discharge, photoionization etc.) generate ample radical species. These significantly increase the overall reactivity for the small fraction of analyte ions present. In general, the rate constants in the latter case are close to the classical collision rate limit and even beyond, due to charge induced polarization effects. It was demonstrated, for example, that in-situ generated OH radicals from dissociated water molecules cause severe post-oxidation effects of the initial ion population and render the interpretation of the resulting mass spectra rather ambiguous [20]. One way of minimizing such ion transformation processes was shown by our group in 2011 [21], by implementing spark discharge lamps in the flow reducing conductance between the high pressure and first differentially pumped stage (cf. section 2) of a MS. This technique successfully proved the anticipated effect by significantly lowering the dwell-time of ions in the collision dominated pressure regime of the mass spectrometer, while still ionizing at elevated gas densities.

In 2011 we filed a patent [19] describing an alternative approach within this particular field of research. Figure 37(a) and (b) depict a sketch of the principal design from the original document and a photograph of the prototype, respectively. Shown is only one half of the device with the milled inner structure, which forms a channel system with the symmetric and complementary second part combined. The key approach is to instantaneously separate ions from a reactive matrix gas flow at the point of origin and guide them into a second gas flow of pure, dry and thus inert nitrogen. Ideally, this should prevent any further reactions with neutral constituents and preserve the initial ion

population. We termed this technique *capillary electrokinetic separation (CESE)*. The crucial part is the rapid transport of charges between two gas flows at the point of contact. First of all, the dimension and contour of this spot necessitate careful adaption to the flow characteristics of the two gas streams to avoid substantial mixing. This can only be accomplished by means of a small aperture between two fast and exactly parallel conducted gas flows, such as in two aligned *capillary* systems. Secondly, in that very moment of ionization a swift *electrical* field driven push/pull pulse is required to efficiently *separate* the ions from the reactive sample flow through a small aperture into the clean nitrogen stream of the MS. Figure 37(c) shows a combination of an exemplary fluid and electrodynamic simulation at a 1.5 mm·1 mm intersecting cross section of two channels, each with 0.5 mm inner diameter. Calculations and data visualization were prepared by Dr. Wißdorf. The blue lines represent single ion trajectories from an initially uniformly distributed population generated in a spot of 1 mm in diameter in the center of the sample flow channel and the pierced upper electrode. The transfer efficiency into the *clean tube* strongly depends on the gas flow velocity, pressure, electrical field strength and length of the applied electrical push/pull pulse. The latter is illustrated in Figure 37(d) for an exemplary set of data with 300 V applied between the extraction electrodes, which results in a maximum at 20 μ s with 60 % efficiency. Shorter pulses lack electrical drag vertical to the gas flow direction and thus ions predominantly remain in the sample flow. Longer pulses result in significant loss by simply pushing the majority of charges against the lower extraction electrode. One essential part for this concept to work is the generation of ions within a very small spot, which was the reason for considering the implementation of the mini spark plasma into the CESE design in first instance. This also allowed synchronization of ionization and extraction. Initial experiments with the prototype from Figure 37 b demonstrated (i) the principal separation capabilities of two intersecting gas flows without substantial mixing, (ii) ion generation with the spark discharge inside the CESE structure and (iii) the impact of push/pull pulses on the measured ion current. However, so far no meaningful separation has been realized since several critical aspects have not yet been resolved technically. First of all the prototype was made of polyvinylchloride for the sake of simplifying the manufacturing process, fully aware of its downsides. Generally, common plastic materials do not provide proper fluid dynamic conductance of ions, and thus charge loss and significant charging effects are the result. Moreover, the impact of the periodically changing electrical field from the spark discharge has not been considered so far and also the adjustment of the two gas flows is critical for operating CESE. The considerable effort required to eventually bring this device into a working condition, in addition to higher priority for other projects with secured funding, suggested to defer further research in this realm. Nevertheless, in the future, with more elaborate 3D-printing techniques available for building advanced inner structures of closed systems this topic will be pursued further.

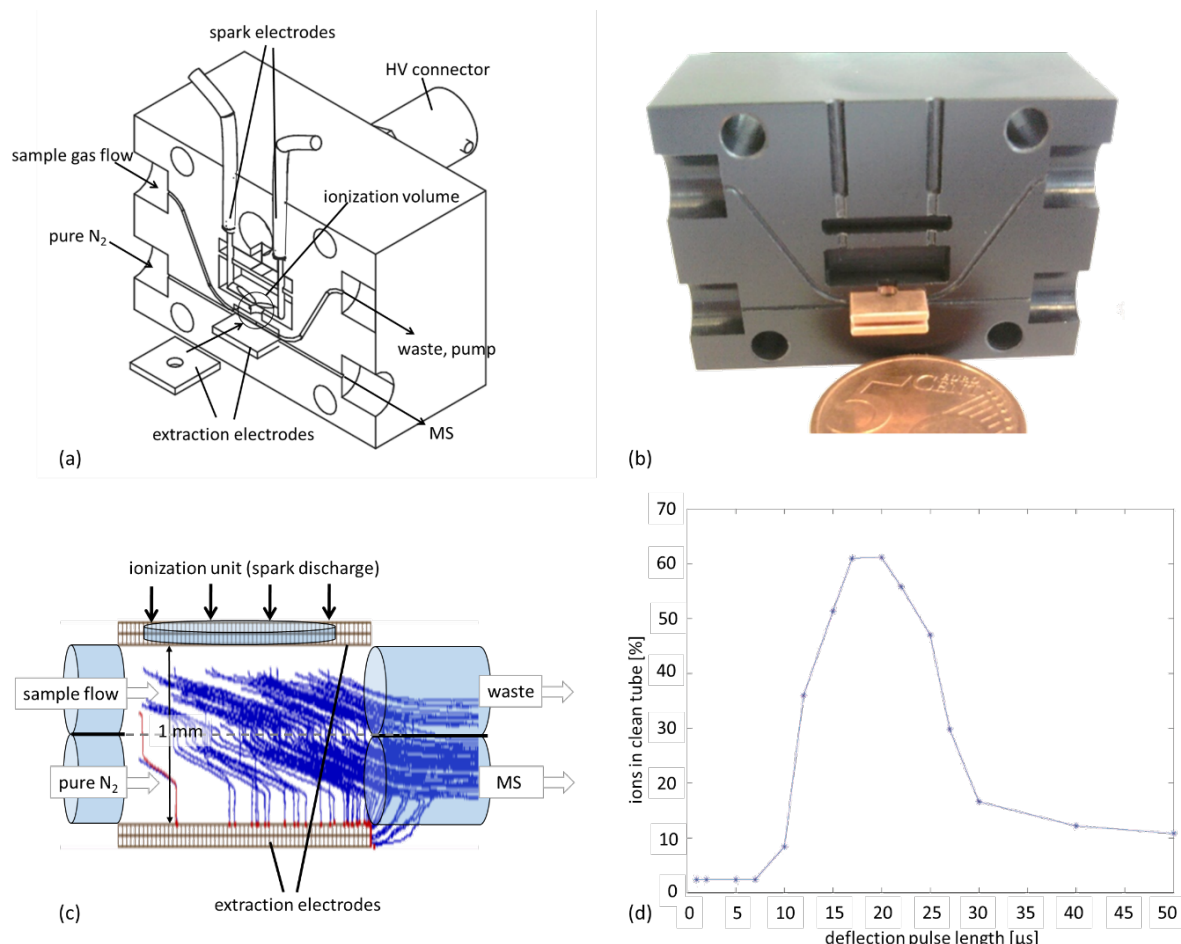


Figure 37: Capillary Electrokinetic Separation (CESE). Ionization and ion transport interface for a mass spectrometer to reduce the extend of ion-molecule reactions at elevated pressures. (a) Original figure from the filed patent, sketching a half section through the device [19], (b) photograph of the prototype (half section), (c) results of an ion trajectory calculation within the CESE device by Dr. Wißdorf and (d) measured ion currents through the clean tube in dependence of applied voltages to the extraction electrodes.

6 Conclusion and Outlook

Over the last couple of years, research based on the developed miniature spark discharge provided numerous new applications, foremost, the spectroscopy covering an exceptional wavelength range from 40 to 1 100 nm. The unique design allows to precisely position the small plasma zone directly into a VUV spectrometer in close proximity to the entrance slit and therefore use the same vacuum housing. With the tube-type electrode assembly the discharge gas composition is swiftly altered exactly in the plasma region without affecting the background gas and also the pressure conditions can be varied within a broad range. All these features allowed to investigate not only the discharge itself regarding typical current/voltage and light emission dependencies, but also to specifically look into the chemistry and physics of particular plasma species. Worth mentioning are the detailed studies on the helium dimer with respect to pressure and gas composition, and the dynamics revealed on the molecular level. For example, population distributions in

combination with exactly calculated potential energy curves of various states were derived for different conditions by fitting the structure of the simulated dimer emission profiles at around 82 nm to the experimental data. Furthermore, the linked datasets of the VUV and UV-VIS-NIR region for *one* specific plasma condition allowed to initiate a unique spectroscopic database to publish full range spectra of various spark plasma conditions. This database allows to compare experimental data of unknown plasmas in the easily amenable UV-VIS-NIR regime (simple fiber optical setup) and estimate the corresponding emission in the more difficult accessible VUV region. This is not the case for other databases, which generally provide only *one* of the wavelength regions for *one* specific plasma condition.

The flexible design allowed to integrate the mini spark into several other applications to make use of the high energy particles. In this regard, concepts of ionization sources for coupling a gas chromatograph with a mass spectrometer or a device to suppress post ionization reactions were developed and tested. However, up to date those remained in prototype state for numerous reasons, above all due to higher prioritized projects with secured funding, in particular in the realm of chapter III HELICAL RESONATOR PLASMA of this work.

Future work with this type of plasma will focus on the expansion of the spectroscopic database. In addition to increasing the variety of available plasma conditions it is intended to redesign the experimental setups and include an IR spectrometer to cover relevant emission in the infrared range as well. This will greatly improve plasma diagnostics, reveal new insights into the state population distribution of highly excited species and aid in investigating their chemical and physical behavior. Furthermore, the conducted high pressure experiments showed greatly enhanced photon fluxes in the VUV region with increasing gas density, however, technical limitations of the spectrometer hampered the assessment of the upper boundary. The intended redesign will expand the high pressure capabilities, accordingly. Lastly, work is planned on aligning the laser light of two already available tunable optical parametric oscillators (OPO) with the spark plasma zone. Both OPOs cover a total wavelength range between 200 and 4500 nm and will allow excitation and de-excitation of specific states for selectively manipulating the plasma composition and the radiative output.

III HELICAL RESONATOR PLASMA

1 Abstract

During the course of *Plasma Research*, the helical resonator (HR) became one of the most intensely investigated and applied plasma sources. To date this field generated a scientific output of nine peer-reviewed publications [131-140], twelve posters [141-152] and four talks [153-156] presented on international conferences, and two commercially available products [157, 158]. These results involved the work of two Bachelor [159, 160], five Master [161-165] and four PhD theses [166-169].

In the mass spectrometry community, a prominent example of this plasma type is the wide spread application in atmospheric pressure photoionization (APPI) mass spectrometry. Typically a copper strand coil with about 120 windings is surrounded by a grounded metal sheath and drives a low pressure plasma inside a gas-tight glass tube, filled with krypton xenon or argon. The generated vacuum ultraviolet radiation is transmitted through a MgF₂ window at one end of the tube. The small power supply driving the resonator operates at 13.56 MHz and requires about 0.5 W with an input voltage of 15 V. With these rather convenient requirements, but persuasive performance in terms of generating ionizing radiation, this setup caught our attention.

Beginning in 2012, as part of a joint research project with a group from the University of Helsinki in Finland, we investigated the spatial emission distribution in the vacuum

ultraviolet region of such a helical resonator driven APPI lamp compared to a DC driven APPI lamp. The results were published in *Analytical Chemistry* in 2012 [131]. In a following two-year long project, funded by Thermo Fisher Scientific (Bremen, Germany), we optimized the overlap of this plasma radiation with the effluent of a gas chromatograph. As a result, a highly sensitive plasma photoionization source with fully maintained gas-chromatographic (GC) performance and optimal ion transfer into a mass spectrometer was designed. Since 2017 this source is commercially distributed worldwide in cooperation with MasCom GmbH and GenTech Scientific [157]. It was presented in three invited talks on international conferences [153, 154, 156], subject to five publications [132-136] and one PhD thesis [168] in cooperation with the University of British Columbia (Kelowna, Canada). Within the scope of a master thesis [161], a modified version with an integrated laser ionization source was built and presented in 2016 [170].

In numerous subsequent projects we focused on controlling and deploying the charged species of HR-plasmas. Of particular interest have been continuous gas-flow systems, operable, wherever possible, with the same driver circuit and coil arrangement as used for the approved gas-tight systems. One bachelor [159] and two master theses [162, 163] first addressed fundamental issues, regarding feasible gases, pressures, possible flow ranges, glass types and dimensions, current outputs, long term stability, charge speciation, applicable coil lengths and alternative, high temperature strand materials. We found promising ways of precisely controlling this specific plasma chemistry to generate, e.g., abundant protonating reagents such as H_3^+ and N_2H^+ . We further extended our research efforts to develop helical resonator plasma configurations for chemical ionization mass spectrometry. Since the working pressure can range between 0.1 and 20 mbar, these systems are largely compatible with the conditions prevailing in first differential pumping stages of typical atmospheric pressure mass spectrometers and with conventional chemical ionization (CI) sources. Due to the use of heated filaments the latter are considerably susceptible to exposure to oxygen, which render them impractical for direct air sampling. Hence in the framework of a master thesis [165] and a current PhD thesis [169], and in cooperation with the Atmospheric Chemistry group of the University of Wuppertal, we replaced the conventional CI source of a commercial mass spectrometer with an HR-system. In 2017 our work on HR also called the attention of the Swiss company ToFwerk AG. Within a three year funded project, a PhD student thoroughly investigated the application of HR-plasma based CI-setups in combination with gas chromatography and time of flight mass spectrometry [166]. In the framework of our joint participation in the EU funded CLOUD-MOTION project at CERN, a second PhD student [167] developed this concept further to a commercially available product [158]. It generated an additional scientific output of three publications [137-139], six poster presentations [145-147, 149-

151] and one talk on international conferences [155]. These works significantly contributed to our present knowledge of this remarkable versatile plasma and its use in an open configuration. Various future avenues are envisioned to continue research in this field.

2 Introduction and Theory

Helical resonator plasmas belong to the group of low-temperature, radio frequency (RF) driven inductive discharges. Numerous fields of application for this type have been reported, e.g., in the semiconductor industry for etching, sputtering and deposition processes [118, 171-173] or in gas analysis of volatile organic compounds to generate the required ionizing radiation from low-pressure plasma tubes. The latter can be found in photoionization detectors (PID), either in simple handheld devices, in gas chromatographs (GC) or in the field of mass spectrometry, particularly as fully integrated ionization sources for atmospheric pressure photoionization (APPI). In these PID applications, typically a thin copper strand coil with about 120 windings is surrounded by a grounded metal sheath, which drives a low pressure plasma inside a gas-tight glass tube, filled with krypton or argon. The required vacuum ultraviolet radiation is transmitted through a MgF_2 or LiF window at one end of the tube. The small power supplies operate at the industrial frequency of 13.56 MHz and require about 0.5 W with an input voltage of around 15 V. With these rather convenient, but persuasive performance, this simple hardware caught our attention in terms of basically two aspects:

- (i) The flexibility of this assembly to be modified and applied in versatile setups and
- (ii) efficient operation in an open plasma flow configuration for chemical ionization (CI).

Figure 38 shows an exemplary geometry of the helical resonator plasma and its driving RF power supply used to generate precursor ions in an open flow system. Here, the solenoid, wound around a polyimide support structure, and the copper cylinder were removed from the original PID circuit board and integrated into the depicted setup. The original, krypton filled light bulb was replaced by a glass tube of 12.7 mm outer diameter (OD), conducting a mixture of hydrogen and nitrogen at flow rates of up to 100 sccm and pressures of up to 20 mbar. Usually, the plasma ignites instantaneously without the need of, e.g., external spark sources, except at the upper pressure boundary. The entire assembly is a well-balanced system with the plasma and its properties as an integral part of the resonant electrical circuit. An additional potentiometer with up to 1 k Ω resistance complements the matching network and allows for fine tuning.

Such modifications inherently requested for detailed investigation on the boundary conditions of the parameters essentially impacting the overall performance. Of vital

interest were the applicable pressure ranges in combination with various gas compositions, the layout of the solenoid and its material, the inner tubing with regard to material and outer diameter, just to name a few.

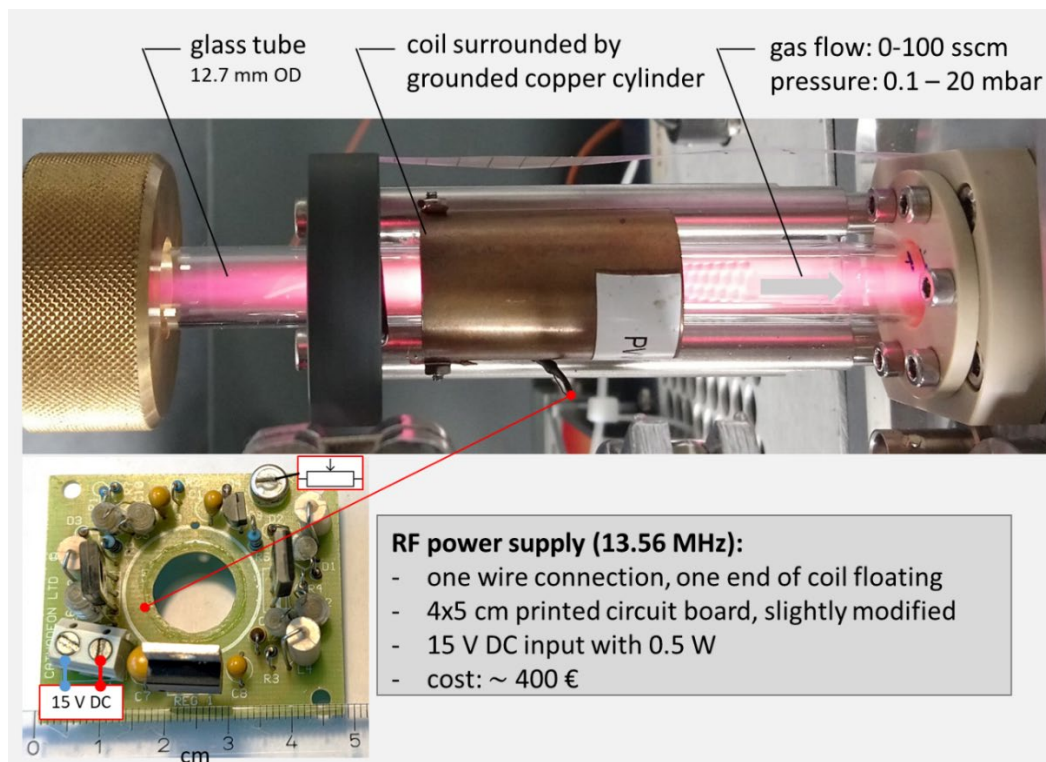


Figure 38: Picture of an exemplary geometry of the helical resonator plasma and its driving RF power supply used to generate particular precursor ions in an open flow system.

Furthermore, in two third-party funded projects one GC-APPI-MS and one GC-CI-MS interface were to be developed using the helical-resonator plasma *radiation* and *ion population*, respectively. The course of these projects will be discussed in detail, including the process of commercialization.

The work presented on the helical resonator plasma is primarily structured as (i) *the use of the radiation* and (ii) *the tailored use of certain plasma ions* provided by this unique plasma type.

2.1 Principle of Operation

In 1831 Faraday published his law of induction, stating that a *change of a magnetic field B* induces a current inside a perpendicularly aligned loop of an electrical wire. Obviously, this current requires a concentrically acting *electrical field E* driving the electrons on a circular path within the wire while the magnetic flux changes. Hence, this law states, that any change of a B -field in time induces a concentrically and perpendicularly aligned E -field. Note, this *inductive electrical field* must be distinguished very clearly from the *capacitive electrical field* generated by spatially separated charges of opposite sign, as

discussed in the theoretical section of the spark discharge (cf. 2.1.1 in II SPARK PLASMA). The induced E -field is independent of the wire being present or not. Consequently, any free electron that happens to be in a plane orthogonally penetrated by an alternating B -field will be forced into a circular motion in this plane. We now consider the magnetic field generated by an electrodeless, RF driven coil as shown in Figure 39.

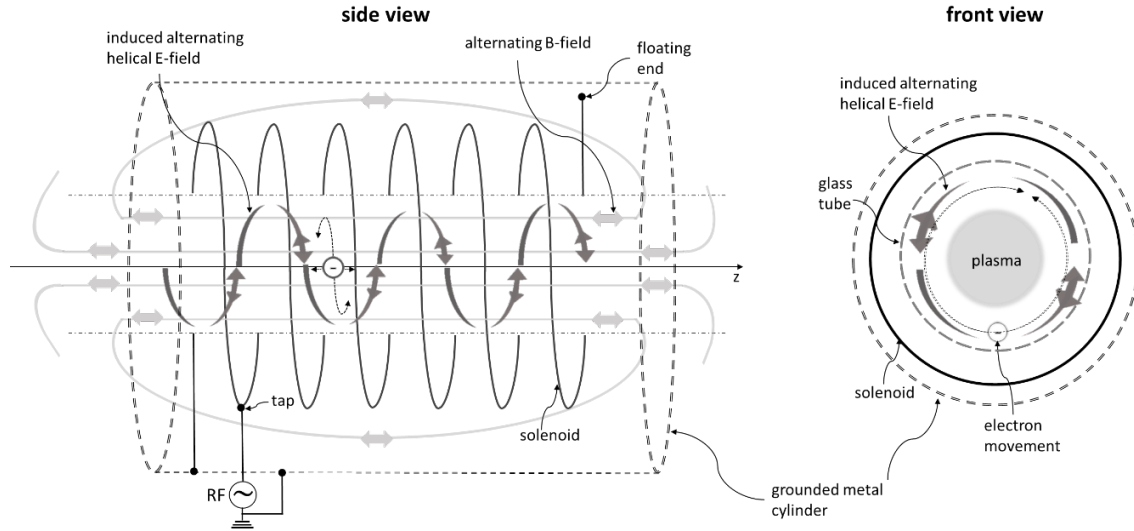


Figure 39: Illustration of the electrical and magnetic fields, and the movement of electrons within the helical resonator.

The alternating B -field induces an alternating electrical E -field inside the coil (*side view*), which forces free electrons in each differential section across the coil axis into a wiggling circular motion (*front view*). Additionally, the change in the magnetic field line density along the z -axis is not zero for an RF driven solenoid, as, for the sake of simplicity, falsely indicated. In contrast, the magnetic field periodically builds up and decays from left to right and vice versa, which generates an alternating B -gradient along the z -axis. By applying the Lorentz force, this causes the electron to additionally move back and forth along the z -axis. The superposition of the orthogonally circular and parallel linear movement results in a helical back and forth motion as illustrated in the side view of Figure 39.

Depending on the charge density of the plasma, electromagnetic fields are more or less shielded from penetrating this region. Consequently, the described electron motion occurs primarily in cylindrically arranged thin layers around the central plasma region as indicated in the front view of Figure 39. Occasionally, these accelerated sheath electrons collide with species from the plasma zone and transfer their kinetic energy into the bulk. This mechanism is referred to as *ohmic heating* and it is the dominant process to transfer energy from the external RF generator for sustaining the plasma. Other mechanisms such as stochastic heating are negligible for the conditions applied in this work. Since the energy transfer into the plasma is based on the motion of electrons within induced

E-fields, this type is also termed *inductively coupled plasma* (ICP). In contrast, *capacitive coupling* is based on *E*-fields generated by spatially separated charges of opposite sign, which basically characterized the interaction mechanism for the spark discharge (cf. 2.1.1.1 in II SPARK PLASMA). However, also in the described RF helical configuration capacitive effects occur, generated by the large potential difference between the two ends of the coil. For nearly five decades after the first observed RF discharges generated with solenoids by Hittorf in 1884, the nature of the coupling mechanism was heavily debated. Today it is well recognized that at higher pressures ($> 2 \cdot 10^{-2}$ mbar) inductive coupling dominates for plasma heating; particularly in the initial electrical breakdown phase the capacitive contribution can be pivotal.

Concepts for predicting the electrical breakdown of helical RF discharges equivalent to the *Paschen Law* for the DC type (2.1.1.6 in II SPARK PLASMA) are not well established. The initial phase requires avalanches of some starting electrons as described in the section *primary amplification* (2.1.1.1 in II SPARK PLASMA). This process is substantially favored by capacitive coupling between the coil ends [174]. The subsequent step in the DC case on the way to a self-sustaining discharge was the *amplification* of the *primary amplification* by means of at least one energetic particle (ion, photon, metastable) from the previous avalanche impinging on the cathode to release at least one further electron as a starting point for the following avalanche (2.1.1.2 in II SPARK PLASMA). This secondary amplification cannot work for a pure electrodeless RF driven ICP. Consequently, a rather simple derivation of some breakdown parameter as function of some other characteristic parameters, such as the breakdown voltage as function of the product of pressure and electrode distance, as presented in the Paschen curves for the DC discharge, is not applicable. However, some corresponding qualitative considerations can be made for the ICP as well. (i) The energy uptake of an electron between two collisions remains a function of the reduced field strength E_R , whether it is a capacitive or an induced electrical field (cf. 2.1.1.1 in II SPARK PLASMA). Thus increasing the induced electrical field strength by increasing the change in the magnetic field in time (increasing the coil current) also increases the kinetic energy of the electrons. The same effect is accomplished by decreasing the pressure. (ii) The operating pressure for a given ICP configuration is mostly restrained to a rather narrow range. Beyond the higher limit the mean energy uptake of the electrons is insufficient to ignite the plasma or balance the ionization and recombination rates in the bulk. The lower limit on the other hand might provide enough kinetic energy, but not sufficient collisions with the background gas. (iii) The gas type/composition with regard to its ionization energy, electron affinity and its general energy deposition function into available degrees of freedom essentially follow the same trends as discussed in detail in the corresponding chapters (cf. 2.1.1.3 to 2.1.1.5 in II SPARK PLASMA). (iv) The role of metastables and photons for plasma ignition and

operation are not as pronounced as in DC discharges due to the missing secondary cathodic effect. In gas compositions with a minor component exhibiting a low ionization energy, the concepts of *gas phase photoionization* and *Penning Ionization*, as discussed in detail in section 2.1.1.4 (in II SPARK PLASMA), still hold true.

As one may have noticed in Figure 39, the RF voltage for the helical resonator as a particular kind of ICP is not simply supplied to one end of the coil, but in a specific tapping position. Moreover, one end of the coil is floating and the other is attached to a grounded metal cylinder, covering the entire assembly. This assembly becomes resonant with a winded wire length matching an integer number of quarter waves of the applied RF wavelength. In this case highly efficient energy coupling into the plasma is obtained. For the specified parameters in Figure 38, 120 windings around a 14 mm in diameter support structure result in 5.3 m total length, which matches the 5.5 m quarter wavelength of the corresponding 13.56 MHz driving frequency quite well.

A rather qualitative picture was presented for the operation and function of the helical resonator, but this is sufficient to provide the theoretical background for the following chapters. Readers interested in more quantitative treatments with corresponding transmission lines, relevance of the tap position, equivalent circuit diagrams and detailed mathematical derivations are referred to related literature [118, 171, 173-176].

3 Use of Radiation

In our investigation, we initially focused on characterizing, optimizing and utilizing the radiation of the helical resonator plasma. Of particular interest were the spatial light distribution of commercially available standard discharge tubes, the development of custom designed discharge tubes, the effect of different glass materials as a dielectric mantle, the impact of coil length, wire material, material of the grounded shield, to name a few. In addition, the development and the process of commercialization of a tailored photoionization source to interface an Orbitrap mass spectrometer with a gas chromatograph will be discussed in detail. Several applications with a prototype will be presented.

3.1 Spatial VUV Light Distribution

In 2012, in cooperation with the Division of Pharmaceutical Chemistry of the University of Helsinki in Finland, we recorded the spatial emission distributions of various commercially available VUV lamps. The aim of the work was to present a detailed comparison between the DC and RF driven vacuum ultraviolet lamps, both commonly used in atmospheric pressure photoionization mass spectrometry [131]. Of particular

interest were notable differences with regard to ionization efficiency and induced ion chemistry, based on each characteristic emission distribution. In the following, only results obtained with the RF lamp are presented, since they merited consideration in the further course of this work. The interested reader regarding the experimental results from both lamp types is referred to Vaikkinen et al. [131].

The discharge tube under investigation was a PKR 106, filled with Kr in the mbar range and driven by the corresponding RF power supply, both from Heraeus Noblelight. A sketch in Figure 40(a) illustrates the lamp and plasma dimensions.

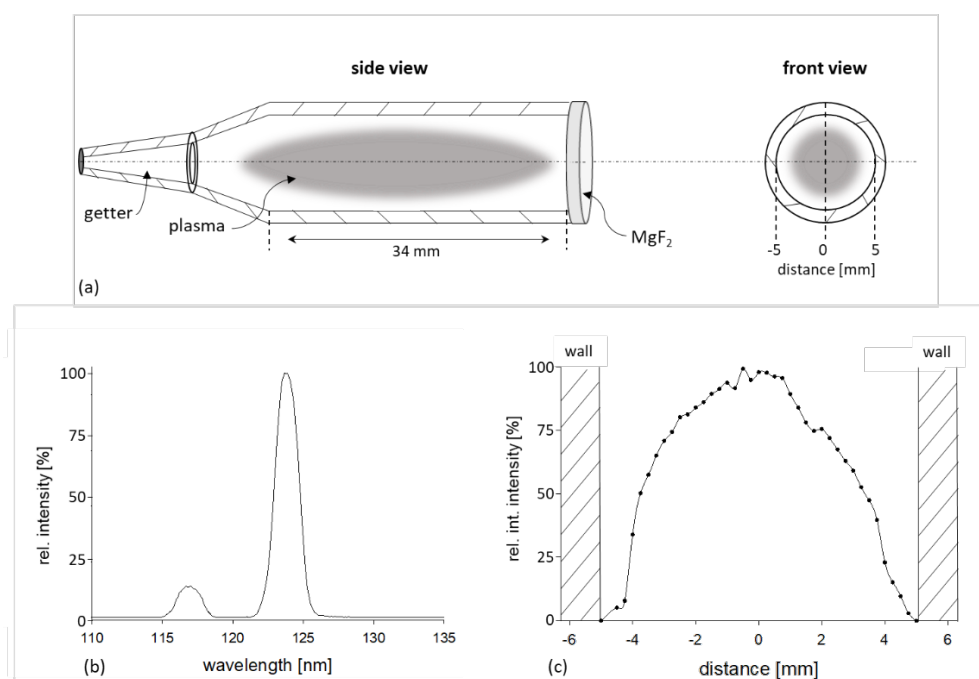


Figure 40: (a) Sketch illustrating the lamp and plasma dimensions of a PKR106 lamp typically used for APPI-MS. (b) VUV spectrum of the krypton filled PKR106 lamp and (c) VUV emission distribution measured across the window diameter, representing the plasma dimension inside the glass tube.

The glass tube has a total length of 55 mm and an outer diameter of 12.7 mm. The wall and window thickness are 1.1 mm and 1.0 mm, respectively, as taken from a broken specimen. This leads to an inner diameter of 10.5 mm. For the experimental part the ARC VM-502 VUV spectrometer (Acton Research Corporation, Acton, MA) as described in detail in section 3.1.4.1 (II SPARK PLASMA) was used. For the determination of the emission distribution along the diameter of the lamp exit window, a custom entrance flange with an embedded, plane and rectangular plastic aperture of 0.25 mm width and 15 mm length was built. The center was precisely aligned with the entrance slit of the spectrometer. An additionally mounted blind flange allowed evacuating the chamber down to $4 \cdot 10^{-6}$ mbar and then pressurizing it with pure helium assuring good VUV transmission conditions. After removing the blind flange, the lamp window was seamlessly positioned in front of the aperture without perturbing the plasma condition. The spectrometer chamber was continuously flushed with helium held slightly above

atmospheric pressure, so that a low gas flow exited the opening and encompassed the window of the lamp. With a translational stage the discharge tube was precisely moved along the entrance of the spectrometer in 250 μm steps. For each position a scan between 110 and 140 nm was recorded (cf. Figure 40(b)), and the total integrated emission of each spectrum (peak areas) was plotted as a function of the window position (cf. Figure 40(c)).

The wavelength spectrum shows the expected peaks at 123.6 nm and 116.5 nm, corresponding to the krypton transitions from $4s^24p^5(^2P^{\circ}_{3/2})5s$ and $4s^24p^5(^2P^{\circ}_{1/2})5s$ to the $4s^24p^6$ electronic ground state, respectively. The relative intensity of the latter accounts to merely 10 %, which is significantly below the listed value of 71 % at the NIST database[177]. With the spark discharge and a mixture of 0.4 % krypton in helium, a relative intensity of 55 % for the 116.5 nm peak was observed (cf. Figure 14). Clearly, the relative population of the excited electronic states largely depends on the prevailing plasma condition, therefore the NIST tabulated intensities as well as the spark spectra are comparable only to a limited degree. Nevertheless, this evidently low fraction is mainly attributed to the use of a MgF_2 window with an extremely steep transmission decrease between the two peaks. Hence, the spectrum in Figure 40(b) does not adequately reflect the true relative population distribution between the two electronically excited states.

As illustrated in the side view of Figure 40(a) the plasma volume is of prolate spheroidal shape, which reflects the zeroth order operation of the helical resonator with one maximum in the center and two minima at each end of the coil. Consequently, the induced electrical field is strongest in the center of the coil and decreases to both ends. The total VUV-emission scan across the window indicates a plasma volume closely bound to the wall with approximately 0.2 mm distance (cf. Figure 40(c)). Note, however, that each point resembles the light emitted from a volume part of the plasma along the length of the discharge tube and that emitting species radiate spherically and uniformly distributed. Therefore, light detected in wall vicinity can partially originate from species in the center with the right orientation to the spectrometer entrance. Nevertheless, the scan results yield a quantitative picture of the usable surface area with appreciable VUV emission within a radius of 4 mm from the center axis. To a good approximation the emission can be regarded as radial symmetrical, with the steepest intensity increase between a radius of 4 and 3 mm from around 5 to 75 %. Between 2 and 0 mm the intensity distribution follows a rather broad plateau.

Since full spectra were recorded, we also looked at the relative peak intensities for each position. A location dependent shift of the population distribution between the two electronically excited states may be an indicator for a non-uniformly distributed electron energy across the plasma volume. However, no such dependency was observed and the relative intensities were essentially the same for all spectra.

As a general remark it is worth to note that the operation of this type of plasma configuration as a VUV-lamp is still far from optimized. Since no reflective layers are used, most of the radiation is simply lost. Future work should focus on different designs, possibly incorporating parabolic, highly VUV-reflecting layers to enhance collimation and focusing of the light towards the application area or volume.

3.2 Photoionization Source for GC-Orbitrap-MS

Initiated in 2012 by Prof. Dr. Makarov from Thermo Fisher Scientific, this third-party funded project aimed at a design of a photoionization source to couple gas chromatographs with mass spectrometers of the high resolution Orbitrap series. Two different irradiation concepts were initially developed, the spark based type introduced in chapter 5.2 (II SPARK PLASMA) and the helical resonator version. The course of the latter design process to market maturity and its launch with MasCom Technologies GmbH in 2016 [157] will be discussed in the following. Several theses [160, 161, 168], as well as oral [153, 154, 156] and poster presentations [141-144] on international conferences accompanied this project and a final summarizing paper was published in 2016 by Kersten et al. [136]. Indicated by the corresponding reference given in the heading, some of the following chapters are partially adopted from this publication.

3.2.1 Theory on Ion Generation in a GC-API Source

Briefly, a rough model is presented to estimate an upper limit of the generated ion concentration of an eluting compound in a GC ion source volume and to identify critical parameters [136]: A compound exits the GC column into the ion source as “packet”, thus maintaining its local concentration. The make-up gas determines the velocity of the traversing packet through the ionization region and hence determines its irradiation time. Any mixing with the make-up gas during the residence time in the irradiated volume is neglected. In addition, any heterogeneous gas velocity distribution within the ion source is also not taken into consideration.

We begin by estimating the mean analyte concentration at the exit of the GC column. If we consider 2 pg on column injection of naphthalene with a molar mass of $128 \text{ g}\cdot\text{mol}^{-1}$, a total number of $9.4\cdot 10^9$ molecules will elute during the chromatographic peak. Discarding peak broadening due to the ion source volume and assuming a chromatographic peak simplified as rectangular in shape with a 4 s base width, we obtain an elution velocity of approximately $2.4\cdot 10^9 \text{ molecule}\cdot\text{s}^{-1}$ for this compound. With a typical column flow of 1.5 sccm or $0.025 \text{ cm}^3\cdot\text{s}^{-1}$, an approximate mean concentration, c_{neutral} , of $9.4\cdot 10^{10} \text{ molecule}\cdot\text{cm}^{-3}$ is derived. The residence time, t , which is identical to the

irradiation time of a molecule in the ionization region, is 8.5 ms, which is calculated by dividing the source volume of 0.12 cm^3 by the transfer capillary volume flow of $14.2 \text{ cm}^3 \cdot \text{s}^{-1}$. Due to the short residence time, we assume that the initial neutral analyte concentration exceeds the generated ion concentration by at least three orders of magnitude after “completion” of the ionization process. Hence, the photoionization rate will be pseudo-zeroth order with respect to the neutral analyte concentration. We thus obtain the following linear equation for the mean ion concentration, c_{ion} , generated during elution:

$$c_{ion} = c_{neutral} \cdot \Phi \cdot \sigma \cdot \varphi \cdot t \quad (15)$$

where Φ is the photon flux of the VUV lamp (typically $10^{14} \text{ photons} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$), σ is the absorption cross section (in this wavelength range, σ is typically on the order of $10^{-17} \text{ cm}^2 \cdot \text{molecule}^{-1}$), and φ is the ionization quantum yield (assumed to be $1 \text{ molecule} \cdot \text{photon}^{-1}$). This yields a final mean ion concentration in the GC effluent of $8 \cdot 10^5 \text{ ions} \cdot \text{cm}^{-3}$. Multiplication by the column flow of $2.5 \cdot 10^{-2} \text{ cm}^3 \cdot \text{s}^{-1}$ leads to an ion current of $2 \cdot 10^4 \text{ ions} \cdot \text{s}^{-1}$, which enters the mass spectrometer. Integration over the 4 s rectangular peak width results in $8 \cdot 10^4$ naphthalene ions, which roughly correspond to the integrated area of the chromatographic peak (discarding ion transfer losses).

Equation (15) suggests two important parameters for efficient ionization, relevant to the design of a GC-APPI interface: (i) The spatial overlap of the neutral sample concentration, $c_{neutral}$, with the photon flux, Φ and (ii) the residence time, t , of the neutral sample in the irradiated volume. First, keeping in mind that the compound packet eluting from the GC column represents the highest neutral sample concentration in the entire setup, the first parameter implies that the compound packet has to be kept tightly intact and as close to the VUV lamp as possible after elution. Second, the residence time in the irradiated volume should be as long as possible without compromising the GC separation performance.

3.2.2 Prototype Development

3.2.2.1 Experimental Equipment

Mass Spectrometer [136]

The GC-APPI interface development focused on coupling the source assembly to the standard API inlet system of Thermo Fisher Scientific (Bremen, Germany) Orbitrap mass spectrometers. For evaluation of the ion source performance, an Exactive Orbitrap MS, and additionally a modified Exactive MS with a compact, high-field Orbitrap analyzer (research-only), were employed [178]. The standard IonMax API housing and the ion sweep cone were removed and the electronic interlock was bridged with appropriate

resistors to mimic an APPI/APCI operating mode. The original transfer capillary was replaced by a stainless steel capillary (0.5 mm inner diameter, Klaus Ziemer GmbH, Langerwehe, Germany), which was modified with a gas tight adaptor connecting to the source assemblies. Special care was taken when tuning the ion optics of the instrument. For this purpose, toluene vapor was added to the make-up gas and automatic tuning on m/z 92 was performed. In order to minimize the 91/92 ratio, i.e., minimizing collisional-induced dissociation (CID) within the inlet region, the voltages in the first differential pumping stage were manually adjusted. The relative intensity of the dehydrogenated cation of toluene is used as a measure for harsh and unintended CID conditions, which arise from excessively strong potential gradients within the lower mbar pressure range. This tuning procedure aims for simultaneously efficient and soft ion transport conditions to enhance the overall chromatographic sensitivity. The standard Exactive MS provided four different mass resolving power settings from 10 000 to 100 000 with intrinsically changing scan rates from 10 to 1 Hz, respectively. This means that the instrument mapped the chromatographic elution profile with sufficient data points only at its lowest mass resolution. The modified research-only instrument, however, operated at a mass resolving power of 30 000 with a scan rate of 9 Hz.

Gas Chromatograph [136]

A TRACE 1310 GC oven equipped with a TR-Dioxin 5MS column (30 m x 0.25 mm ID x 0.1 μ m), both from Thermo Fisher Scientific, was employed for chromatographic separation. A heated transfer line (Thermo Fisher Scientific) was used to transfer the GC effluent from the oven to the APPI interface.

Light Source [136]

A commercially available, low-pressure krypton plasma lamp with a 13.56 MHz electronic driver from Syagen (Santa Ana, CA, USA) provided VUV radiation at 10.0 and 10.6 eV (cf. spectrum in Figure 40(b)). The RF driver is compatible with the MS instruments electronics and software. It is noteworthy that in all the designed GC-APPI interface versions the driver unit was exposed to extreme heat due to its spatial vicinity to the hot surfaces of the ion source assembly (cf. Figure 42). Nevertheless, during the entire development period the lamp emission did not suffer from any noticeable intensity loss or variation. In an experimental study, which spanned two months of extensive use, the integrated emission output between 200 and 1 000 nm was monitored with a UV-VIS-NIR fiber optical spectrometer (AvaSpec-3648, Avantes BV, Apeldoorn, The Netherlands) at different ambient conditions. The recorded intensity variation was below 10 % and correlated well with the VUV emission intensity, provided that the VUV light transmission properties of the MgF_2 window of the lamp remained constant as well. The stability of the VUV radiation output is a prerequisite for the analytical reproducibility.

3.2.2.2 Results and Discussion

The GC-APPI development phase consisted of four iterations, in the following denoted as #I – #IV. Table 2 lists essential parameters and characteristics for each development step. Figure 41 shows a cut through the central ionization region of each of the first three versions and Figure 42 shows a drawing of source assembly #IV with a close-up of its ionization volume.

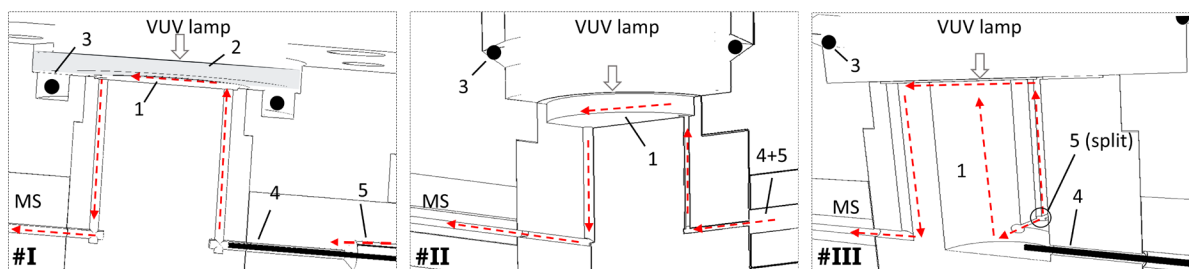


Figure 41: From left to right, the first three iteration steps of the GC-APPI interface development: 1. Ionization volume, 2. MgF₂ window, 3. O-ring, 4. GC-column and 5. make-up gas

Iteration #I

Initial experiments were conducted using a comparably small cylindrical ionization volume of 5 mm³, an irradiated area of 50 mm², and a height of 0.1 mm (cf. Figure 41, #I). The GC column and the sheathing make-up gas (N₂ with 99.999% purity, Messer Industriegase GmbH, Bad Soden, Germany) were guided directly into the heated source body. The make-up gas was adjusted with a 1 slm MKS mass flow controller and multigas controller 647C from MKS Instruments Deutschland (München, Germany). The diameter of all gas-flow channels was 0.5 mm, matching with the diameter of the transfer capillary in the MS. A MgF₂ window with 1.5 mm thickness (Korth, Altenholz, Germany) and a standard Viton O-ring sealed the ionization volume. Although LiF has higher transmission properties in the VUV region around 10 eV, MgF₂ is far less prone to heat stress and radiation-induced color centers (solarization). The window of the VUV lamp was seamlessly surface-mounted to the MgF₂ window. The apertures of the source enclosure (transfer capillary entry, make-up gas/column connector) were O-ring sealed. Instead of a straight flow direction, technical design restrictions required an inverse U-type of flow with four sharp turning points (cf. Figure 41, #I). This seems to be against common sense concerning dead volumes and particularly ion wall losses. However, injections of headspace acetone revealed Gaussian shapes of the chromatographic peaks with ≤ 6 s base peak widths. The design of version #I, however, did not show the targeted femtogram level sensitivity; a 1 µl injection of 1 ng·µl⁻¹ naphthalene in hexane was below the LOD.

Table 2: Characteristic properties of each GC-APPI source version.

source version	I	II	III	IV
source body material	aluminium	aluminium	aluminium	Invar36
ionization volume [mm ³]	5	60	100	120
make-up gas [ml·min ⁻¹]	600	600	600 (split flow)	600 - 850
irradiation time [ms]	0.5	6	10 - 20	12
additional MgF ₂ window	yes	no	no	yes
sealing material	Viton	Viton	FFKM	MgF ₂ window cemented and coated with mineral sealing; graphite flat gaskets
surface finishing	no	No	no	polish and electrochemical gold coating
LOD of naphthalene [pg on column]*	1ng on column not detected	1	0.1	0.01**
peak-width (base) [s]	6	3	3	< 2
peak shape	Gaussian	Gaussian	Gaussian	Gaussian
linear dynamic range	not measured	5 - 500 pg R = 0.995	0.16 - 500 pg R = 0.998	0.01 – 1 000 pg R = 0.998

* Extrapolated to the mass spectrometric signal-to-noise ratio of S/N = 3 based on the lowest concentrated injection. The noise level was determined by Qual Browser software.

** The instrument setup was a modified Exactive MS with a compact, high-field Orbitrap analyzer and an S-lens interface.

Iteration #II

The poor sensitivity performance of #I was primarily attributed to the small irradiation volume. This volume was thus enlarged 10-fold in version #II. Furthermore, the additional MgF₂ window was removed, which reduced the VUV transmission by up to 10 %. Instead, the window of the VUV lamp was directly attached to the surface of the ionization volume and O-ring sealed to the source enclosure (cf. Figure 41, #II). To minimize the transfer time to the ionization region, the GC effluent and the 600 sccm make-up gas were premixed upstream in a make-up adapter (Valco fused silica make-up adapter, 724FSMUAS15L, Machery-Nagel, Koblenz-May, Germany). The mixture flowed through the 0.5 mm channel making several turns before entering the transfer capillary. The N₂ make-up gas from compressed gas cylinders was further purified with a VICI Metronics (Poulsbo, WA, USA) N₂ purifier to sub-ppbv levels of impurities as stated by the manufacturer. The complex geometry of the source was again imposed by the required arrangement of the GC, the MS, and the make-up gas adapter. Nonetheless, this setup retained the Gaussian GC peak shape and the base peak width was decreased by a factor of two to ≤ 3 s, as recorded with 100 pg naphthalene on column. With version #II, the LOD for naphthalene was approximately 1 pg on column, based on the extrapolated mass

spectrometric signal-to-noise (S/N) ratio, with the noise calculated by the Xcalibur Qual Browser 2.2 software (Thermo Fisher Scientific). The linear range obtained for naphthalene was over two orders of magnitude (5 to 500 pg on column) with a regression coefficient of $R = 0.995$. The major drawback of version #II was the relatively high background of chemical noise and limited source temperature of $\leq 150^{\circ}\text{C}$, both caused by standard Viton O-rings used as sealing material.

Iteration #III

Four major changes were introduced when designing version #III (cf. Figure 41, #III): (i) implementation of high-temperature O-ring seals, (ii) placement of the GC column exit port into the ionization volume, (iii) splitting of the make-up gas flow, and (iv) a further enlargement of the ionization volume. The newly implemented FFKM O-rings (V075B, Westring Dichtungstechnik GmbH, Köln, Germany) allowed source temperatures of up to 325°C and showed good form stability throughout a long-term test at maximum temperature. Nevertheless, the seal closest to the ionization volume around the glass body of the VUV lamp (cf. Figure 41, #III) led to permanent mass spectrometric interferences due to outgassing. This contamination effect appeared at source temperatures exceeding $\sim 250^{\circ}\text{C}$ and dominated the mass spectrum throughout the entire chromatographic run with a group of signals centered at $m/z \sim 366$. The second change enhanced the overlap of the analyte concentration and the photon flux. Direct infusion of the effluent into the irradiated volume replaced the premixing step of make-up gas and GC effluent from version #I and #II. Similarly, the introduction of a make-up gas split was intended to reduce the flow rate in the ionization region, thus leading to higher sample concentrations and longer residence times in the irradiated volume. Roughly two-thirds of the total make-up gas flow was introduced at the bottom of the ionization volume to support the transport of the GC effluent toward the VUV lamp and one-third was guided toward the VUV lamp in a separate channel (cf. Figure 41, #III). The combined gas streams exited the source via a capillary channel with two U-turns before entering the transfer capillary. The analytical performance of version #III was investigated at 250°C source temperature to keep the background noise at an acceptable level. The chromatographic fidelity of version #II was retained, again with Gaussian GC peak shapes of base width of ≤ 3 s at 100 pg naphthalene on column. A linear range of 160 fg to 500 pg naphthalene on column was obtained with a regression coefficient of $R = 0.998$ and an LOD of 100 fg.

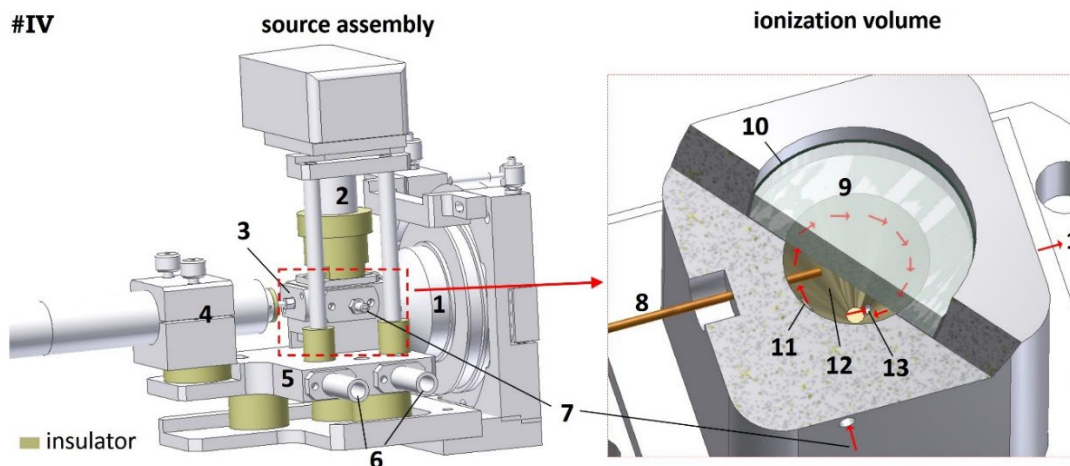


Figure 42: GC-APPI source interface #IV: 1. MS, 2. VUV lamp, 3. GC column adapter, 4. GC transfer line assembly, 5. heater table, 6. heater cartridges, 7. make-up gas adapter, 8. GC column, 9. MgF2 window, 10. sealing with cement and inorganic coating, 11. make-up gas inlet, 12. conical ionization volume, 13. exit to MS.

Iteration #IV

A new fluid dynamic concept was introduced in the final prototype version #IV. The ionization volume is conically shaped with the exit port to the transfer capillary located at the apex, parallel to the GC column entrance port (cf. Figure 42; indices 13 and 8, respectively). Matching the spatial emission-profile of the VUV lamp (cf. Figure 40(c)), the circular cone base diameter is 8 mm; the lateral height of the cone is 7 mm, which results in an ionization volume of 120 mm^3 (cf. Figure 42; index 12). The GC column and the N_2 make-up gas entrance ports are located directly below the window; the latter is asymmetrically positioned to the far left of the cone and perpendicular to the GC column, as shown in Figure 42, indices 3 and 7, respectively. The GC entrance port is 0.4 mm closer to the window than the make-up gas entrance. Computational fluid dynamic (CFD) simulations, as shown in Figure 43(a), support that in this configuration the main gas flow creates a sustained vortex inside the irradiated volume. The simulated massless particle traces of the GC flow in Figure 43(b) visualize the vortex drag exerted on the GC eluent, which results in a helical motion towards the apex. From a fluid-dynamic perspective, version #IV addresses the main issues concerning preservation of chromatographic fidelity and the key factors in equation (15). As discussed, this equation states that with longer time t , a higher concentration of neutral analyte c_{neutral} , will reside in a more densely irradiated volume, represented by Φ , and more analyte ions will thus be generated. For this reason, the eluent exit port in version #IV is positioned as close as possible to the (divergent) radiation source. Secondly, the rotational symmetry of the velocity distribution along the z-axis balances the temporal overlap of the GC peak and the irradiation time. While the temporal overlap of neutral analyte density and the photon flux is maximized with small velocity vectors in the x,y-plane as well as in z-direction, the irradiation time is increased with a larger x,y-velocity contribution, as it supports a

circular movement with increasing radius. Furthermore, the simulated y,z -velocity vectors in Figure 43(b) reveal virtual absence of back flow contributions. This translates to a zero dead volume configuration and preservation of the primary peak shape as provided by the chromatography. This is confirmed by experimentally determined peaks of Gaussian shape and base width < 2 s (cf. Table 2).

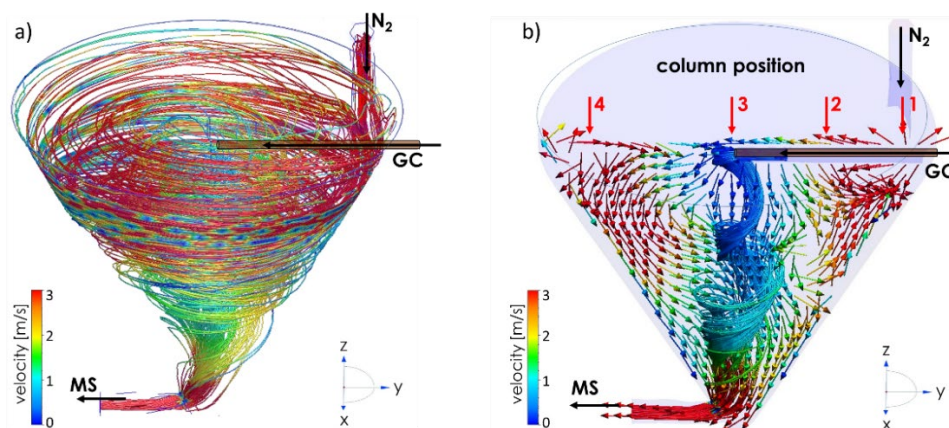


Figure 43: (a) Massless particle trace simulation of the make-up gas inside the conical ionization volume of version #IV. (b) Massless particle trace simulation of the GC eluent inside the conical ionization volume of version #IV. Additionally, the simulated velocity vectors in the y,z -plane are shown.

Experiments at different GC column positions gave some insight into the impact of the flow profile on the detected ion population. Figure 43(b) depicts four different column positions at which 10 pg naphthalene on column were injected, with three replicates at each position. At position 3, the analyte elutes exactly at the center axis of the vortex with a y -velocity magnitude of $0.5 \text{ m}\cdot\text{s}^{-1}$. In theory, this should be the optimum for the temporal overlap. However, in the experiments at this position only 20 % of the maximum attainable mass spectrometric response is reached. This is readily explained by the comparably small irradiation times. As illustrated in Figure 43(b), virtually all velocity vectors in the center of the y,z -plane are small in magnitude; however, they also point directly to the apex, with only very low momentum in the x,y -direction. Positions 1 and 4 represent the other extreme with the analyte eluting close to the boundary of the vortex into a factor of six faster angular make-up gas velocity. This results in extended circular motion in x,y -direction with correspondingly increased irradiation times at the cost, however, of increased eluent dilution and possibly higher ion wall losses. Positions 1 and 4 gave similar results with roughly 80 % of the maximum attainable intensity. These results strongly support the simulated rotational symmetry of the gas flow within the source. Maximum intensity was obtained in position 2, with the column located 2 mm off the center axis, reflecting an optimum balance between eluent confinement and irradiation time.

From a technical point of view, version #IV was the most advanced. As demonstrated by the results obtained with version #III, even the highest temperature-resistant O-rings were not appropriate for the desired source cleanliness. Alternatively, the optical mount in #IV was attached with inorganic materials. First attempts to cement the VUV-lamp body directly into the source enclosure, however, failed due to mechanical strength. Thus, the concept of installing an additional window, at the cost of roughly 10 % radiative loss, was re-invoked, with the benefit of having a much simpler and more rugged assembly. A MgF_2 window of 12.7 mm in diameter and 1.5 mm thickness was cemented (Omega® CC High Temperature Cement, OMEGA Engineering, Inc., Stamford, CT, USA) into a 13 mm wide and 2 mm deep recess of the source enclosure (cf. Figure 42; indices 9 and 10, respectively). The enclosure itself was made of invar36 to match the small thermal expansion coefficient of the cement and MgF_2 . With a cone base of 8 mm, the window and the enclosure formed a relatively large, highly polished annular contact surface of roughly 2.5 mm in width. Experiments with several different cements revealed severe leakage for all cements at temperatures above $\sim 180^\circ\text{C}$, presumably due to increasing porosity. Repeated application of additional thin layers of an inorganic chromium oxide coating (Ipseal Khaki, Indestructible Paint, Ltd., Birmingham, UK) on the cement substantially reduced the leakage issue (cf. Figure 42; index 10). All remaining joints, such as the MS capillary adapter, the make-up gas adapter and the GC-column adapter were sealed with Sigraflex graphite flat gaskets (A.W. Schultze, Geesthacht, Germany). A standard GC graphite ferrule connector established a gas tight connection between the GC column and the column adapter.

In version #IV, particular attention was paid to the surface inside the ionization region, since plain invar36 tarnishes and corrodes at higher temperatures to a nearly black-stained surface. The cone was thoroughly polished and then electrochemically gold coated. Attempts with gold sputtering failed primarily due to the cone apex regions poor accessibility, which resulted in inhomogeneous gold layers. Furthermore, the sputtered gold did not prevent the ionization region from turning black after heating the invar36 material to 300°C . The electrochemical approach with a gold electrolyte solution from Conrad Electronic (Hirschau, Germany) generated a solid and smooth gold layer. While extensive use of the ion source (24/7 at 325°C for four months) did result in loss of brilliance, the gold layer prevented the cone from turning black and the surface remained smooth. The reflectance of electropolished gold coatings may reach 12 % in the applied VUV range [179]; the efficiency of the electrochemical approach presented here is assumed to be below this value. It was speculated that a substantial increase of the surface reflectivity was attainable with an Al/MgF_2 double layer coating, which according to Hass et al. may reach up to 80 % at 120 nm [180]. Unfortunately, an attempt with physical vapor deposition (PVD) of 200 nm and 25 nm thick layers of aluminum and MgF_2 ,

respectively, did not lead to the expected reflectivity increase. Due to the substantially higher effort and cost compared to the gold coating process, the PVD approach was not further pursued.

To avoid inhomogeneous electrical fields due to possible charging processes inside the capillary system, the path downstream of the ionization volume was made of a uniform 0.5 mm ID metal duct without any insulating material separating the MS metal capillary and the source enclosure. This design requires that the entire source block and heater table (cf. Figure 42; 5) floats on the MS transfer capillary voltage, an essential parameter for reasonable ion optics settings in the first differential pumping stage. Consequently, several electrical insulators were arranged around the ion source to maintain grounded mechanical mounts.

The analytical performance of version #IV was thoroughly evaluated using a modified Exactive MS with a compact, high-field Orbitrap analyzer [181]. A wide range of compounds, including compounds covered under several EPA methods (EPA 8081, EPA 527, EPA 8270, AOAC Method 2007.01), were analyzed. In total 195 of 209 tested compounds, including but not limited to pesticides, FAMES, phthalate esters, semi-volatiles compounds, aliphatic hydrocarbons, fragrances, and flame-retardants, were detected. The linear range for most compounds spanned five orders of magnitude from 10 fg to 1 ng on column with regression coefficients of $R = 0.998$ and inter-run reproducibilities of <30 % RSD. Gaussian peak shapes with base widths of as low as 2 s were obtained.

In several subsequent joint projects, this prototype was broadly used in our lab. In cooperation with a Canadian group from UBC Okanagan, the analytical performance was extended by the use of unusual dopants such as CS₂ [132, 168]. With a group from the University of Helsinki (Finland), the prototype was used to investigate ionization mechanisms in direct and dopant-assisted atmospheric pressure photoionization and atmospheric pressure laser ionization. For these studies the setup was extended by a frequency-quadrupled diode-pumped solid-state (DPPS) Nd:YAG laser operating at 266 nm (4.66 eV) wavelength, a spot size of 0.5 mm, a pulse energy of 200 μ J, and a power density of 10^8 W·cm⁻². The laser beam pointed straight into the cone, sweeping past the exit of the GC-column. The results were presented in three joint papers [133, 134, 182].

3.2.3 Transfer to Market Maturity

The convincing performance of the prototype propelled our decision to introduce a comprehensive concept to our project partner and continue the way of launching a commercially available GC-APPI version. This initial market design integrated the

developed “vortex” source into Thermo’s common IonMax® housing line, as depicted in different views in Figure 44.

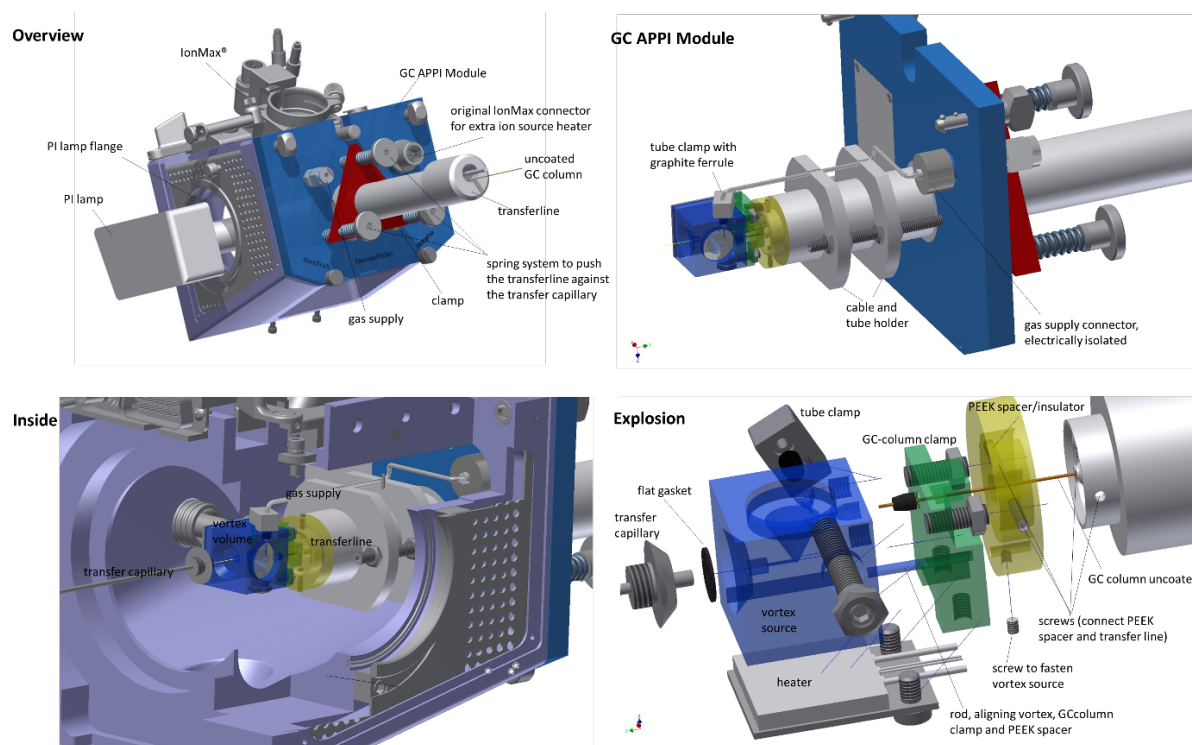


Figure 44: Design for the implementation of the GC-APPI source into the original IonMax®.

Compatibility with most of the original MS infrastructure was important to enable swift exchange of ion sources and to operate the GC interface with existing voltage supplies and software control. Hence, in this design the front plate of the IonMax® body had to be removed and replaced by the GC-APPI module, which was mounted on an extra flange with all gas connectors and electrical feedthroughs included. A triangular clamp held the transferline in place, allowed precise alignment and provided the necessary pressure to seal the vortex source against the MS transfer capillary. Standard GC ferrules and a carbon based flat gasket ensured gas tight and clean conditions, an essential prerequisite for low background noise and stable operation. To maintain the vortex chamber at temperatures of up to 350°C, a small and flat ULTRAMIC® heater from WATLOW® (Watlow Industries, Hannibal, MO, USA) was considered at the bottom. In typical MS operation, the transfer capillary is electrically biased to several volts, which required a deliberate electrical isolation concept. The entire vortex block had to be at the same bias voltage to prevent a potential barrier in the transition region, while the remaining setup was held at ground potential. Charge losses due to such barriers were found to be significant in small channel systems. Therefore, this design considered an additional PEEK spacer between the transferline and the GC-column clamp, and an electrically isolated gas supply connector on the base plate. For the VUV radiation generation an original helical resonator power supply, compatible with the IonMax® housing, is inserted from the left side, with the rare

gas lamp directly positioned on the MgF_2 window of the vortex source. An additional PEEK spacer (not shown) ensured electrical isolation to the RF power supply. For this design special care was taken for very clean conditions, such as usage of non-outgassing materials, a gas tight source volume and very clean make-up gas, ideally using an additional cartridge filter.

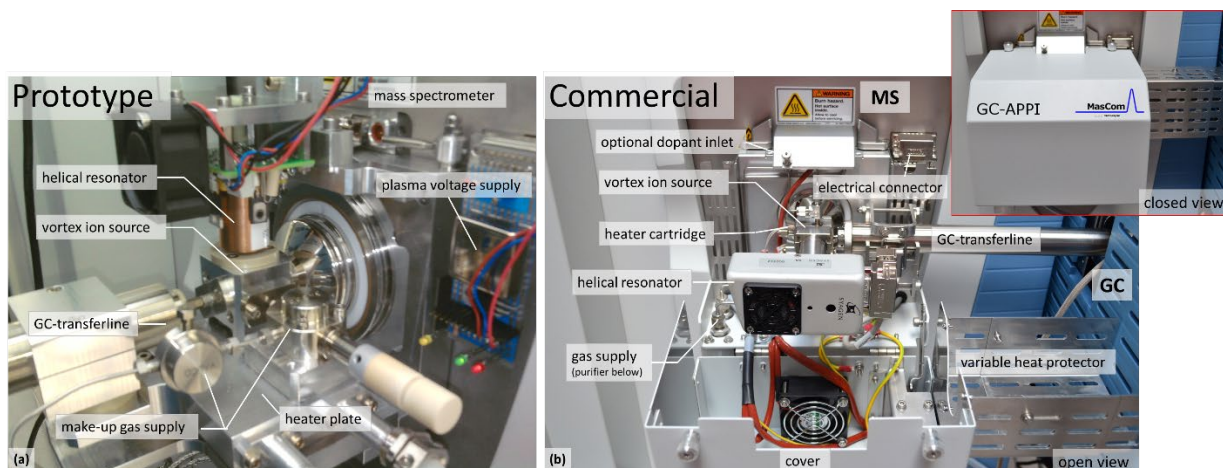


Figure 45: (a) Picture of the GC-APPI-MS prototype interfaced to an Exactive Orbitrap in our lab, (b) final commercially available GC-APPI-MS source as distributed by MasCom GmbH [157].

Thermo Fisher agreed to launch a commercial GC-APPI version, however, demanded a more user friendly side-by-side configuration of the mass spectrometer and the gas chromatograph. Since the IonMax[®] housing does not provide the necessary ports, a completely new and designated version was required. At this point the further process to market maturity was outsourced to MasCom GmbH in Bremen, Germany. In close collaboration, based on our experience regarding key operational parameters, critical dimensions and materials, Kai Meyer from the company Rosemeier & Meyer (Ing.-Büro für Grafik und Konstruktion GbR, Bremen, Germany) was assigned to finalize the commercial version. The result is shown in Figure 45 in comparison to the prototype. Essential changes were made by (i) lining up the MS and GC in a side-by-side configuration, (ii) inserting heating cartridges into the source block, (iii) using gold-wire sealing between the MgF_2 window and the vortex source (not shown), and (iv) covering the entire assembly for safety reasons.

Since the launch in 2016, several of these units have been successfully sold worldwide by MasCom Technologies GmbH and GenTech Scientific. A number of publications in various fields of application appeared in the literature. Detecting chemical signatures of poultry pest [183, 184], investigations of the water quality of the Rimac River in Peru as one of Lima's main water sources [185], detecting doping metabolites in urine samples [186] or studies of crude oil fractions [187] are just examples of publications in recent years using the GC-APPI developed during this project [188-196].

3.3 Combined Plasma and Laser Ionization

In this project we combined the GC-MS adapter for plasma photoionization (APPI) described in chapter 3.2 with a laminar-flow concept for atmospheric laser ionization (APLI) introduced by Kersten in 2011 [197]. It uniquely allows the irradiation of a GC effluent with VUV (123.6 nm and 116.5 nm) and UV (248 nm or 266 nm) light to drive single (SPI) and resonance enhanced multiphoton ionization (REMPI) schemes, respectively. The latter is a rather selective but highly efficient way to ionize preferably highly conjugated molecules with strong absorption in the UV range [198]. In contrast, a broad range of compounds is amenable to SPI with the krypton plasma emission used. Incorporating both techniques into one design was challenging in the way that they operate at best at rather contrary conditions in combination with a GC setup and the typical gas flows prevailing in AP-MS systems. The divergent, continuous VUV lamp radiation requires close and precise alignment of the gaseous analyte effluent with respect to the lamp window (cf. 3.2.2). The pulsed, parallel laser radiation, on the other hand, offers optimum ionization efficiency with an analyte distribution along the beam path to allow for multiple light pulse exposures. In both modes the chromatographic fidelity has to be sustained, which requires a thorough heating concept and particular attention to avoiding dead volumes.

During his master thesis in 2015, Dr. Kroll successfully developed and thoroughly characterized such a dual-mode device for a Bruker MS inlet geometry [161]. This work was presented at the ASMS conference in St. Louis, MO, USA in 2015 [170]. The drawing shown in Figure 46 illustrates the setup.

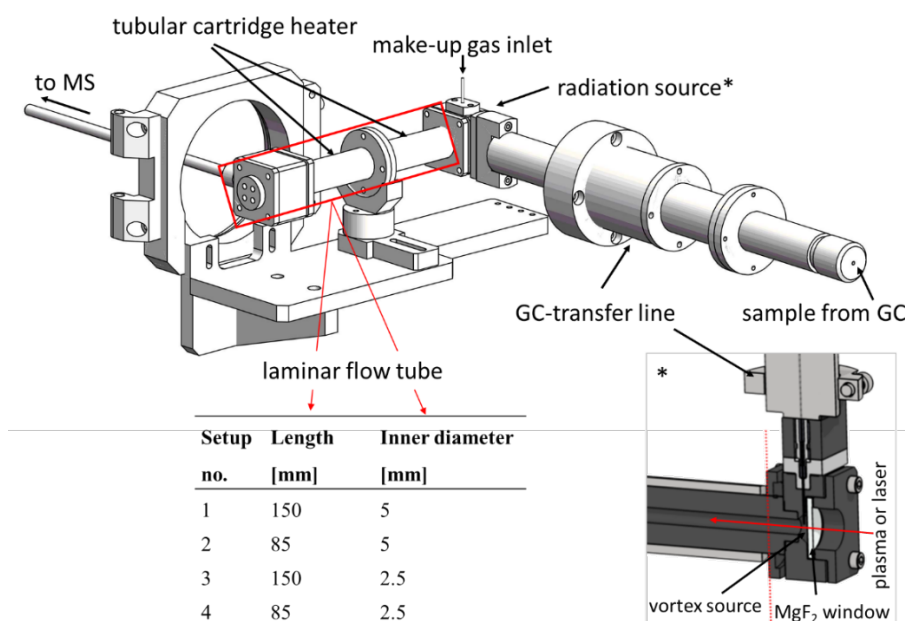


Figure 46 adopted from [161]: Illustration of the combined plasma and laser ionization source for GC-MS.

A heated transfer line guides the GC-column to the adapter of the vortex source (cf. 3.2.2), which allows precise alignment with the GC-effluent within the established whirling make-up gas. Either the light of a Kr-plasma (Morpho Detection, Tustin, CA, USA) or a pulsed KrF*-excimer laser operating at 248 nm (ATL Lasertechnik, Wermelskirchen, Germany) were used to irradiate the ionization region through the MgF₂ window. For optimizing the ionization efficiency with the divergent plasma radiation, only the volume and thus the flow conditions closest to the window are critical. On the contrary, the laser beam requires exact alignment along the entire volume of the connected laminar flow tube to facilitate multiple pulsed light exposures of the sample.

A modular design allowed changing the tube length as well as its inner diameter, resulting in four different setups to scrutinize these parameters with respect to sensitivity and overall chromatographic performance. Some analytical results of this work are presented in the diagrams and the table of Figure 47.

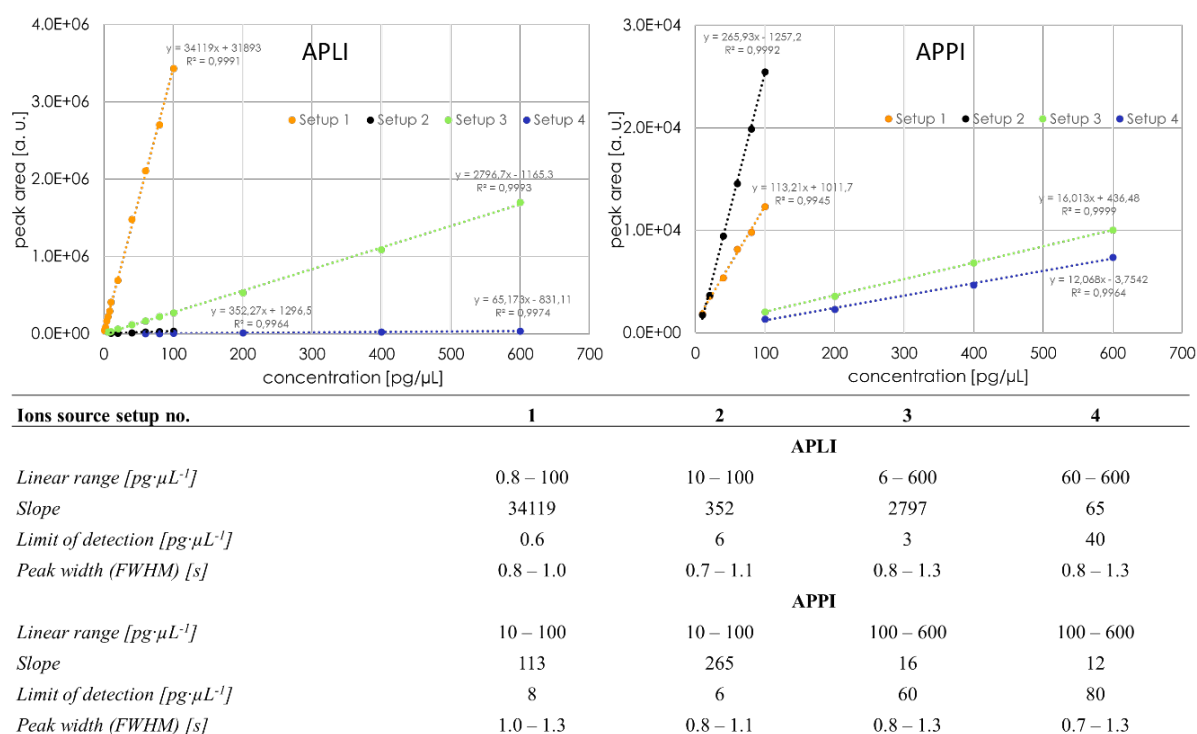


Figure 47 adopted from [161]: Experimental results demonstrating the analytical performance of the combined GC-APLI and APPI MS setup for different tube length.

A dilution series of naphthalene was injected into the GC and the sensitivity, limit of detection and peak width were derived for each setup with both ionization methods. Typically, the unfocused laser operated at 500 Hz repetition rate and 10 mJ pulse energy with a duration of 5 ns. Apparently, in nearly all configurations APLI surpasses the APPI performance with respect to LOD and sensitivity, except for no. 2, for which similar results were obtained. As expected, the longer versions no. 1 and no. 3 benefit from the extended irradiation volume in case of APLI with LODs of 0.6 and 3 pg·μl⁻¹, respectively. The factor of five difference is attributed to the increased wall loss in case of the 2.5 mm as compared

to the 5 mm inner diameter. The performance of APPI, on the other hand, is rather unaffected by the tube length, but depends significantly on the tube diameter. Halving the latter reduces the LOD by an order of magnitude. Surprisingly, the chromatographic fidelity was not an issue at all. Neither the larger inner diameter of 5 mm nor the tube length of up to 150 mm resulted in significant peak broadening or tailing. Excellent gaussian shaped peaks of around one second width at fwhm were observed in all cases.

3.4 VUV Lamp and Coil Variations

Low pressure VUV lamps similar in design and operation as the one shown in Figure 40(a) have been around for more than eighty years. Among a vast variety of VUV sources, they were initially used in research areas such as photochemistry or photoelectron spectroscopy, motivating substantial work to continuously improve the spectral purity, brightness, and experimental applicability [199]. Over the last five decades, however, more advanced techniques for generating high energy radiation have emerged [200]. Synchrotrons and others reduced the application field for the relatively simple low pressure plasma lamps to photoion detection devices such as handheld VOC detectors, gas chromatographs or mass spectrometers. Over the years, this trend caused less scientific and economic interest for further development. The latest publication describing in detail procedures of building enclosed low pressure plasmas as VUV sources is from 1969 [199]. Today, only a limited number of companies is specialized on producing such lamps with rather limited options. Detailed knowledge about manufacturing procedures is mostly proprietary. However, predefined dimensions and gas fillings of commercial devices essentially limit their integrability and applicability in experimental setups. The same holds true for the power supplies available on the market. Usually, the RF driver circuit and the coil holding the lamp cylinder are integrated into one, rather bulky setup, built from materials that are not suitable for applications requiring, e.g., higher temperatures.

As part of the DFG project [2], experiments investigating the performance of various lamp designs were conducted. This chapter provides an overview of the preliminary and essential experiments performed exploring specific limitations of customized lamp embodiments and RF driver coils. These experiments were conducted using the low-power RF supply detailed in section 2 and pictured in Figure 38.

3.4.1 Custom-built VUV Lamps

In 2017, during her master thesis [162], Kirsten Haberer worked on procedures to prepare VUV lamps with various gas mixtures and varying gas pressures. All lamps were scrutinized with respect to plasma ignition behavior, wavelength resolved light emission and aging. She also investigated glass tubes differing by their dielectric loss factor, a

number relating the fraction of energy from a penetrating RF field lost as heat in the material. Figure 48 illustrates the used setup. Glass tubes of 110 mm length and a nominal outer diameter of 12.5 mm underwent a midsection reduction to 4 mm. This reduction facilitated the melting process of the lamp body. Following this preparatory step, these tubes were affixed into a vacuum-sealed LiF window-mount at one end and a gas-mixing unit at the other. The latter unit consists of a turbomolecular pump, along with two gauges and several needle valves. This configuration allows evacuating the glass tubes to pressures of $1 \cdot 10^{-7}$ mbar, as well as precisely pressurize them with plasma gases ranging between 1 and 200 mbar. In order to carry out plasma ignition experiments and preliminary tests before initiating the lamp melting procedure, the RF power supply underwent modifications to ensure a seamless fit around the glass tubes. This involved enlarging the aperture in the circuit board and rewiring multiple cables (cf. Figure 38). For the final stage of the melting process, a rotatable knob was fastened to the stainless-steel rim of the window mount. This setup allowed the entire assembly to revolve, thereby guiding the controlled melting process along the tube axis. This mechanism is illustrated in Figure 48 as the *glass-melting skid*. The required heat for this procedure was supplied by a standard household butane torch.

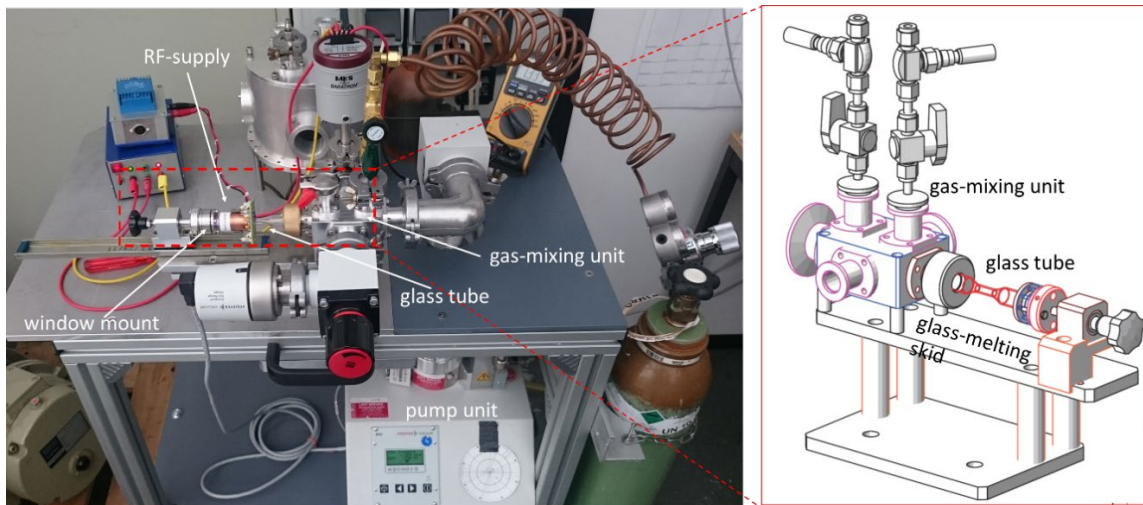


Figure 48 adopted from the final project report [2] to the DFG: Picture and drawing of the setup used for preparing plasma lamps.

The plasma's ignition response concerning pressure was as expected. The breakdown for helium as well as argon started at around 0.7 mbar whereas mixtures of both gases reduced this minimum pressure to 0.4 mbar. The maximum pressure threshold achievable with this specific low-power RF supply was around 20 mbar. Generally, the operating pressure for a given ICP configuration is mostly restrained to a rather narrow range, as discussed in section 2.1. Above the higher limit the mean energy uptake of the electrons is not sufficient to ignite the plasma or balance the ionization and recombination rates in the bulk. The lower limit on the other hand could provide enough kinetic energy, but not sufficient collisions with the background gas. Furthermore, the role of metastables

and photons for plasma ignition and operation are not as pronounced as in DC discharges due to the missing secondary cathodic effect. Of course, in certain gas compositions with a minor component exhibiting a low ionization energy, the concepts of *gas phase photoionization* and *Penning Ionization* still hold true. This was shown by the moderate reduction of the minimum breakdown pressure by 0.3 mbar with the mixtures of helium and argon. In her work Ms. Haberer also investigated the pressure range in which a helium plasma was maintained once it had been ignited. She started at 1 mbar, increased the pressure stepwise and assessed the light emission in strength, spatial expansion and temporary instabilities by simple visual inspection. Surprisingly, up to 60 mbar the stability was nearly unchanged and even at 130 mbar a weak, but nevertheless clear plasma glow was still observed. Between 60 and 130 mbar the brightness steadily decreased, flickering increased, sometimes the plasma extinguished for a second but ignited back again reproducibly. The radial extension continuously decreased down to the center of the glass tube. As a result: Once ignited, the gas density can be increased by nearly an order of magnitude without extinguishing the plasma. An investigation was conducted involving two different glass materials: DURAN® (Borosilicate 3.3) and Glass 8252 from Schott AG (Mainz, Germany), having dielectric loss factors of $3.7 \cdot 10^{-4}$ and $1.1 \cdot 10^{-4}$, respectively. The results, however, showed no discernible influence on the ignition or plasma behavior.

Furthermore, Ms. Haberer thoroughly investigated the finally sealed lamps with regard to their wavelength resolved light emission. She used the VUV spectroscopic setup as described in detail in section 3.1.4 (chapter II SPARK PLASMA). The outcome of this investigation proved to be intriguing yet simultaneously posed a source of frustration. From our spectroscopic experience with the spark plasma, we expected at least production of some radiation of the characteristic 104.8 nm and 106.7 nm transitions for lamps with pure argon or with helium/argon mixtures (cf. Figure 14 and Figure 16). Due to the low pressure conditions we did not anticipate the Ar_2^* dimer to form in noticeable amounts. Also, fully aware of the missing getter material - though its importance was stressed by Gorden in his publication from 1969 [199] - we expected some residual lab air and consequently the typical impurity lines of oxygen, nitrogen and hydrogen as observed several times during the spark experiments (cf. Figure 17, Figure 18, Figure 19). However, irrespective of the type of gas composition or filling pressure, all recorded VUV spectra showed the same structure - with varying intensity - as exemplarily shown in Figure 49 for a helium/argon mixture (1 %) at a total pressure of 8 mbar. No prior measure such as cleaning the glass tubes (heating), changing the sealing material or even purifying the gas changed the appearance of this spectrum. Neither the argon, nor the common impurity lines were observed in this wavelength region. Even more astonishing: The spectrum shown in Figure 49 exactly matches the argon lamp spectrum (without

getter) from the 1969 publication [199]. Gorden did not further assign the individual lines and just mentioned impurities as their source, which completely vanished after having activated the getter material. However, these lines are not just due to the presence of impurities. The entire spectrum from 1 000 up to 3 200 Å shows a clean band structure of the 4th ($A^1\Pi \rightarrow X^1\Sigma^+$) and 3rd ($b^3\Sigma^+ \rightarrow a^3\Pi$) positive system of pure carbon monoxide (CO), apparently without any other compound present. The assignment of the individual transitions in Figure 49 was made according to the spectra reported by Hatta [201]. The fact that carbon monoxide dominates the spectrum in this particular plasma environment has been observed in two independent scientific studies conducted nearly 50 years apart, but the reason for this result is still up for debate. Only the initial gas purity is excluded. The same gas cylinders and mixtures were used with the spark plasma and CO band structures have never been observed in these experiments. In order to evaluate the impact of residual lab air, Ms. Haberer also built lamps filled with helium with 5 % of lab air added at 1 mbar and 20 mbar total pressure, respectively.

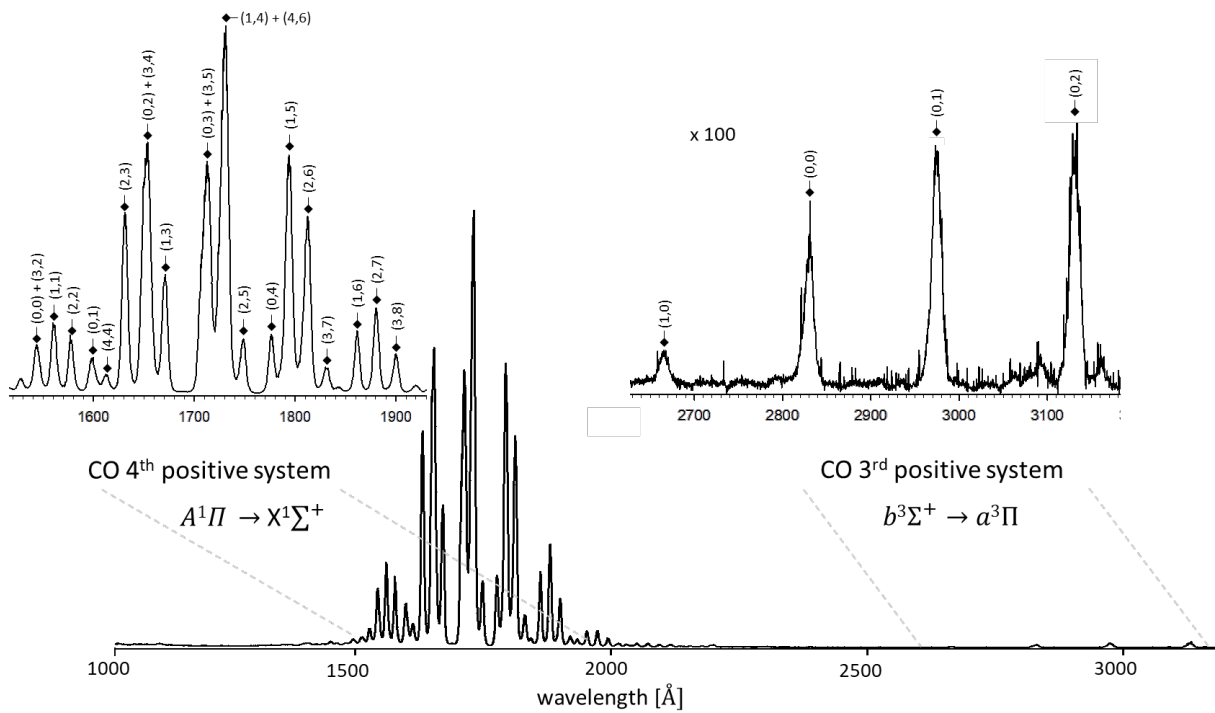


Figure 49 (data recorded by Mrs Haberer [162]: VUV spectrum of a custom made plasma lamp filled with 99 % helium and 1% argon at 1 mbar total pressure. The spectrum is dominated by the characteristic band structures of carbon monoxide. Virtually no other emission is present.

In the lower pressure case, CO remained the dominant light emitting species in the VUV range but the intensity did not increase. In the 20 mbar case, CO nearly vanished and oxygen and in particularly nitrogen monoxide became the main emitting species. The spectrum looked alike the spectrum recorded in the DC plasma experiment with 19 mbar lab air, as shown in Figure 23 with the pronounced NO ($A^2\Sigma^+ \rightarrow X^2\Pi$) band structure. This is compelling evidence that residual lab air is not the source of the presence of ample

CO. Interestingly, we came across two additional research works from entirely different areas of study. However, despite their distinct focuses, they both dealt with a similar plasma setup. These papers also reported the same unexpected phenomenon of carbon monoxide being dominant in the vacuum ultraviolet part of the recorded electromagnetic spectrum. In 1995, Li worked on plasma sources for etching processes with a 1 % CF_4 in helium mixture [202], while in 2010 Lomaev et al. applied a plasma to pure natural gas. In each case carbon monoxide was initially not present. Lomaev et al. even showed the temporal evolution from zero intensity up to a steady state concentration. In both works carbon compounds were added, however, not oxygen, but in the end CO dominated the VUV as it did in our results. All experimental setups maintained the plasma inside a glass tube with favorable surface to volume conditions at pressures in the mbar range. Li explained his results with the interaction of C atoms from the dissociation of CF_4 and oxygen released from the glass walls by fluorine atom etching processes. The latter is a commonly applied method in the semiconductor industry for structuring Si-O surfaces of wafers and releasing volatile SiF_4 . Similar arguments for the carbon and oxygen source to form abundant CO may apply to the experimental conditions by Lomaev et al. as well. Since their gas was composed of 92 % methane, C and H atoms should abundantly form in the plasma volume, the latter interacting with the Si-O surface to generate SiH_4 and release oxygen atoms for the further formation of CO. Hence, we speculate a similar, rather efficient heterogeneous reaction between plasma atoms/radicals and the Si-O surface to have occurred in our VUV lamps. However, the source of the carbon still remains mysterious. Ms. Haberer used a membrane/turbopump combination, which should not impose serious carbon entry through, e.g., pump oil.

In summary, this chapter brought about a sense of frustration due to the failure of achieving the desired level of spectral purity for producing our own VUV lamps. However, it also turned out to be exceptionally captivating to delve into the efficient process of carbon oxidation, mediated by the Si-O surface. Moving forward, further research in this field will need to focus on incorporating additional getter materials, as emphasized by Gorden half a century ago [199]. Additionally, it is essential to further pinpoint the key parameters in these plasma systems that contribute to the effective generation of carbon monoxide.

3.4.2 Investigation on Coil Parameters

In 2018, Mr. Sahling conducted research for his master's thesis, exploring the potential and constraints of operating commercial VUV lamps by making modifications only to the coil unit [163]. These modifications were made while retaining the same RF driver circuit board, as depicted in Figure 38. The main focus was on studying coils with different

numbers of turns, and the impact of the grounded metal cylinder on the stability and intensity of the plasma. During the course of his work Mr. Sahling ascertained valuable parameters under which the plasma was maintained.

The entire coil unit was taken off the board, and it was observed that the length of the wire connecting the RF supply with the coil did not affect the plasma properties. This finding has proved extremely useful in shaping the design for its application as a chemical ionization source, since it allowed for highly compact plasma assemblies, as will be discussed in chapter 4. In addition, when combined with ceramic-coated wires that are wound directly around the glass tubes, active heating of the plasma zone up to several hundred degrees Celsius becomes possible without damaging any sensitive electronic parts. Such a configuration offers a new field of research related to high and extreme low temperature dependent plasma properties of PID lamps. This aspect is also strongly recommended to be taken into account in a potential improvement of the commercial photoionization source for the GC-Orbitrap system, as shown in Figure 45. Here, an actively heated plasma zone may significantly improve the performance particularly regarding high-boiling compounds.

Mr. Sahling carefully examined how the length and number of turns in the coil, when used in combination with metal cylinders of different sizes and materials as the grounded shield, influenced the plasma behavior. He noticed that a reasonably broad range of coil turns, spanning from 75 to 120 windings, which corresponds to coil lengths ranging from 2.99 to 4.79 m (with a lamp diameter of 12.7 mm), effectively sustain desirable plasma conditions. Furthermore, it was revealed that the inner and outer diameters, as well as the mass of the cylinder, are not as crucial. However, it is noteworthy that using stainless steel is not as effective as copper or aluminum. This observation is attributed to the significantly smaller electrical conductivity of stainless steel, which can be up to two orders of magnitude less compared to the other metals. Additionally, it was observed that once the plasma was ignited, the grounded shield could be removed without extinguishing the plasma. It was also feasible to have only the coil wrapped around the lamp body and just hold a metal piece near the coil to initiate the plasma inside. In these experiments, he also identified resonances in the RF driver current, which were influenced by the position of a simple metal rod oriented to the coil axis, as illustrated in Figure 50. Displacement of the rod along a 75-turn version caused a single resonance in the drawn current near the floating end of the coil. On the other hand, with 90-turns, two resonances were observed, one close to the RF input and one exactly at the floating end of the coil. The precise nature of these resonances remains uncertain. However, it was also observed that the increase in current did not exhibit a linear correlation with the VUV output. In fact, elevating the current, for example, from 20 mA to 100 mA, resulted in only a modest 2 % increase in ionizing radiation. Therefore, these resonances are not directly pertinent to optimizing

the plasma in its capacity as a PID. Nevertheless, they still remain an interesting subject for future enquiries.

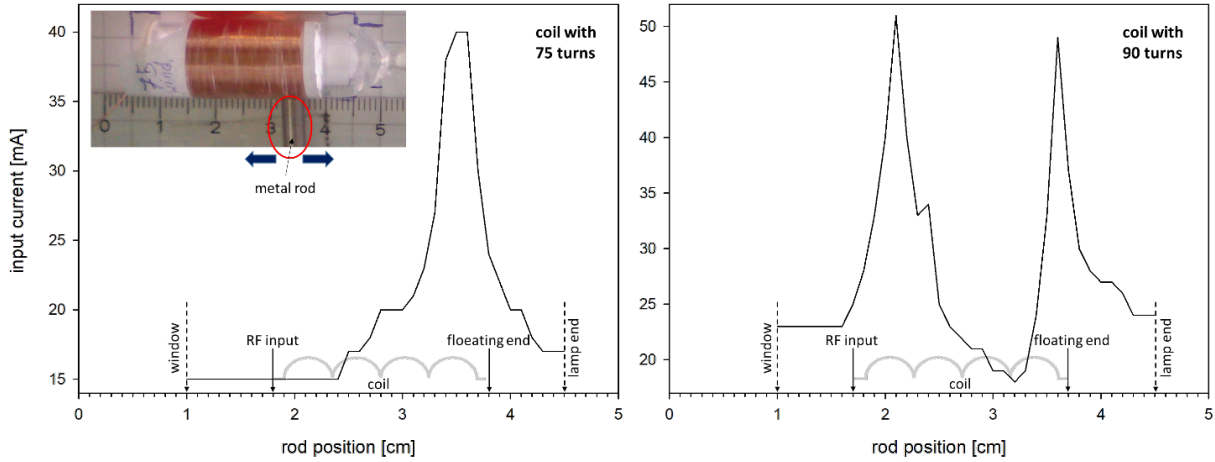


Figure 50: Data and picture adopted from Mr Sahling's work [163]: Illustrating the effect on the HR input current upon placing an external metal rod along the HR coil.

3.4.3 Additional Topics Worth of Further Investigation

The following section briefly touches on some more theoretical thoughts and incidental observations that appear worth of being addressed in future research.

3.4.3.1 Impact of External Magnetic Fields

By chance we noticed considerable axial displacement of the plasma zone with additional magnetic fields positioned in close vicinity to the front of the PID lamps. In most cases the light emitting volume was shifted towards the window, which significantly increased the usable radiative output. This is favorable for PID applications, as, e.g., in the developed GC-APPI-Orbitrap system (cf. Figure 42). For the latter, however, care must be taken since the required high temperature exceeds the Curie-Temperature of most magnets. Also, pronounced degradation of the window or the sealing material through the plasma proximity should be examined carefully.

3.4.3.2 Impact of Materials Inside the Plasma Volume

In a series of investigative experiments, a grounded copper coil was positioned inside a sealed glass tube that contained helium at various pressures. The visual results are depicted in Figure 51, where one can observe a plasma region taking on the shape of the coil. As the pressure decreases from approximately 9 mbar to 0.5 mbar, the plasma zone becomes increasingly dense around the coil. Independent of their usefulness, the nature and dependencies of this effect are interesting to be explored further, e.g., by applying additional DC or even RF voltages to the inner copper coil with defined phase shifts to the

driving main RF. Also, the impact of different metals and their shapes are worth to be explored.

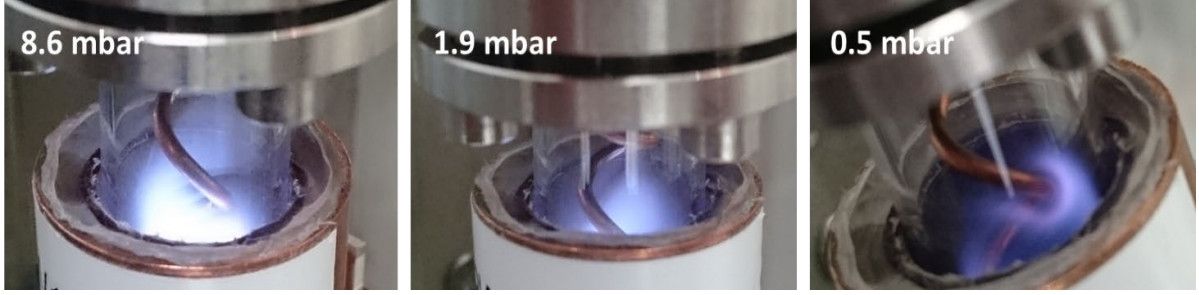


Figure 51: Pictures of an HR-helium plasma at different pressures perturbed by an inserted copper coil.

3.4.3.3 Metastable Depopulation for Increased VUV Emission

The abundance and importance of metastable species in plasmas should not be underestimated as pointed out in Chapter II (SPARK PLASMA) in sections 2.1.1.4 and 3.2.2.2. These sections provide insight regarding the essential role of metastable species for understanding phenomena as decreasing breakdown voltages and the generation of highly excited ions when a secondary gas is introduced. Figure 52(a) shows the emission spectrum of a commercial krypton PID lamp (PKR 106, Heraeus Noblelight GmbH, Hanau, Germany) in the range of 300 to 950 nm, recorded with a high resolution iHR320 spectrometer (HORIBA Ltd., Kyoto, Japan).

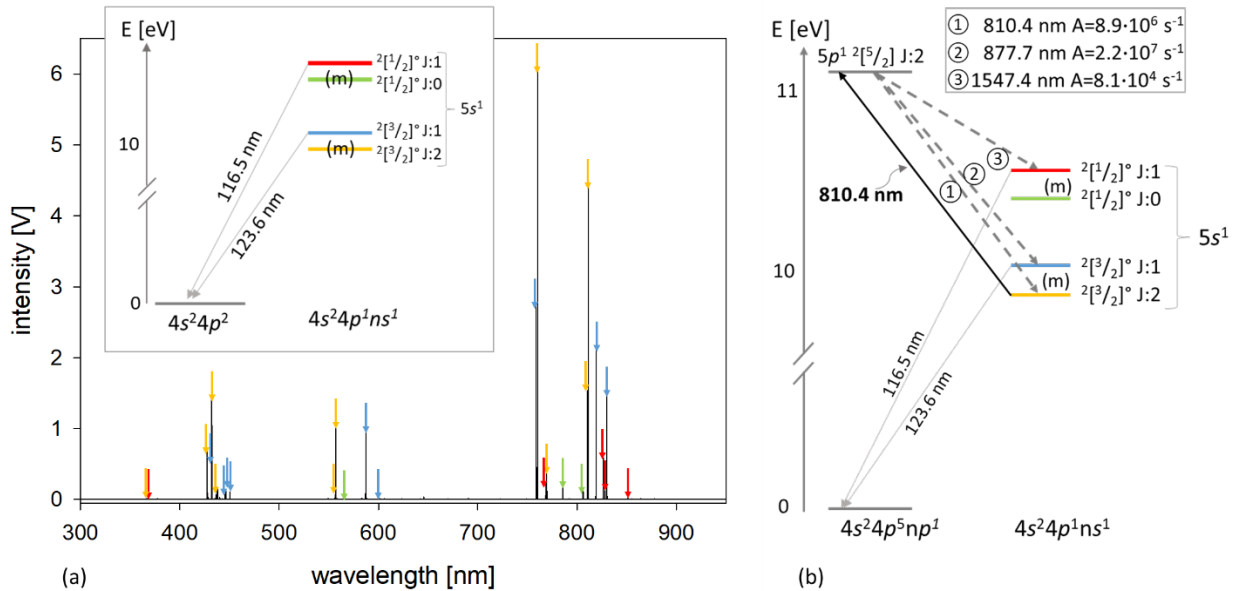


Figure 52: (a) Emission spectrum of a commercial krypton PID lamp in the range of 300 to 950 nm, recorded with a high resolution iHR320 spectrometer. The colored arrows indicate observed transitions ending in one of the four lowest excited states of the Kr-system, as shown in the inserted diagram. Two of these states (marked blue and red) radiate with emission of the characteristic 123.6 nm and 116.5 nm photons, and the other two (marked orange and green) are metastable (m). (b) Illustration of a feasible scheme to radiatively depopulate the metastable $2[3/2]^o J:2$ excited state in favor of the 123.6 nm radiation.

This spectrum indicates the presence of abundant metastables in this RF plasma. Nearly 99.5 % of all observed peaks are assigned to transitions into the four levels of the $5s^1$ electron configuration of krypton. Of these, all transitions into the two metastable states $2[3/2]^\circ J:2$ and $2[1/2]^\circ J:0$ are marked by orange and green arrows, respectively. Blue and red arrows highlight the observed transitions into $2[3/2]^\circ J:1$ and $2[1/2]^\circ J:1$. As illustrated by the level diagram in Figure 52(a), these two states are coupled to the ground state upon emitting the characteristic VUV radiation at 123.6 and 116.5 nm (cf. VUV spectrum in Figure 40(b)), respectively. With a rough estimate based on the spectral intensities and the respective Einstein coefficients A [177] one can derive a relative population of approximately 61 % in the first ($2[3/2]^\circ J:2$; metastable; marked in orange), 36 % in the second ($2[3/2]^\circ J:1$; marked in blue), 2 % in the third ($2[1/2]^\circ J:0$; metastable; marked in green) and 1 % in the fourth ($2[1/2]^\circ J:1$; marked in red) excited state. This estimate neglects (i) direct excitation into these states, (ii) electron induced transitions between them and (iii) the radiative decay in the VUV for the two allowed transitions. Nevertheless, this finding strongly suggests that in this dynamically equilibrated RF plasma a substantial fraction of krypton can be found in a metastable state. It is appealing to explore whether the VUV photon flux can be increased by deliberately depopulating these metastables. This approach is not only of interest with regard to the use of this lamp as a photoionization source, but also in terms of fundamental principles in plasma dynamics. The enrichment or reduction of certain species in such an environment, by means of external parameters, may also allow us to control the involved chemistry and physics paving the way to new insights and applications. One possible approach to reduce the abundance of a certain excited state is through optical quenching. In the literature this technique is commonly used to distinguish between the physical and chemical properties of different metastables by selectively removing one species [203-205]. For our purpose, Figure 52(b) illustrates a feasible scheme to depopulate $2[3/2]^\circ J:2$ excited species in favor of the 123.6 nm radiation. Therefore, photons of 810.4 nm from a strong external light source are absorbed to drive the transition into the $2[5/2]^\circ J:2$ excited state with a $5p^1$ electron configuration. Subsequently, three radiative relaxation pathways are possible, indicated by the circled numbers and dashed arrows: (i) The transition back into the initial metastable state with an Einstein coefficient of $A = 8.9 \cdot 10^6 \text{ s}^{-1}$, (ii) decay into the $2[3/2]^\circ J:1$ state by emitting photons of 877.7 nm with a rate of $A = 2.2 \cdot 10^7 \text{ s}^{-1}$ and (iii) decay into the $2[1/2]^\circ J:1$ state with 1547.4 nm radiation at a rate of $A = 8.1 \cdot 10^4 \text{ s}^{-1}$. The contribution of the latter is negligible with a nearly two orders of magnitude lower coefficient as compared to the others. The second route is the most advantageous and results in the subsequent release of the desired 123.6 nm radiation.

In her master thesis, Ms. Schuler was the first to work on this topic [164] in our group. Employing a tunable laser of the optical parametric oscillator type (NT342 Series,

EKSPLA, Vilnius, Lithuania), she irradiated a krypton as well as a xenon plasma with different wavelength matching the respective transitions for various depopulation schemes such as the one exemplarily shown in Figure 52(b). There was no experimental configuration possible allowing for the direct measurement of the VUV radiation utilizing a spectrometer and irradiating the plasma with the laser at the same time. Therefore, we monitored the ionizing radiation by recording the photoion current generated in a toluene-saturated gas flow passing the PID lamp with a Faraday cup, which was connected to a sensitive transimpedance amplifier (PS-15-25-L, FEMTO® Messtechnik GmbH, Berlin, Germany). Unfortunately, within the restricted time frame of the thesis work, we were not able to stabilize the base photoion current to a level at which a modulation in dependence of the irradiation wavelength could be observed. Ongoing work in this realm focuses on alternative detection methods for the VUV emission, such as ozone production or recording a photoelectron current. The use of strong, continuous radiation sources instead of a pulsed laser will also be scrutinized. For example, a laser diode with nominal emission at 808 nm, commonly found in diode-pumped Nd:YAG solid-state lasers, could be employed. Through temperature adjustments the diodes offer the flexibility of wavelength tuning up to the required 810.4 nm for the discussed quenching scheme.

4 Use of Plasma Ions

Considerable research effort has been dedicated to control and utilize the helical resonator plasma as a source for abundant H_3^+ ions. This strong gas phase acid has been of particular interest to our group as a precursor for chemical ionization. When a setup is designed and operated with due care this acidity can be “adjusted” in subsequent reactions to tailor the reactivity of the primary proton donator to the specific analytical needs. Throughout this work, we focused on using the helical resonator in its configuration shown in Figure 38, despite the fact that substantially denser plasma types and more powerful supplies are available. The reasons for this approach were pivotal to us when designing new instrumentation with a plasma source from scratch: (i) The RF circuit board is a low cost device, its layout is open source and can easily be reengineered and modified. (ii) In terms of space and power requirements the demands are extraordinarily low compared to other systems and (iii) its robustness and stability were already demonstrated in the work using the VUV emission (cf. Chapter 3).

4.1 Preliminary Work

In her master thesis in 2016 (cf. chapter 3.4.1), Ms. Haberer additionally paved the way for using the helical resonator configuration in open flow systems, which represents the

basis for a plasma driven chemical ionization source [162]. She investigated the pressures and gas flows that could be applied with a persistently stable radiative output. In 2017, Mr. Kutsch began scrutinizing species-resolved ion fluxes [159]. As part of his bachelor thesis, he coupled a hydrogen-fed helical resonator plasma to a molecular beam Hiden HPR60 quadrupole mass spectrometer, as depicted in Figure 53(a).

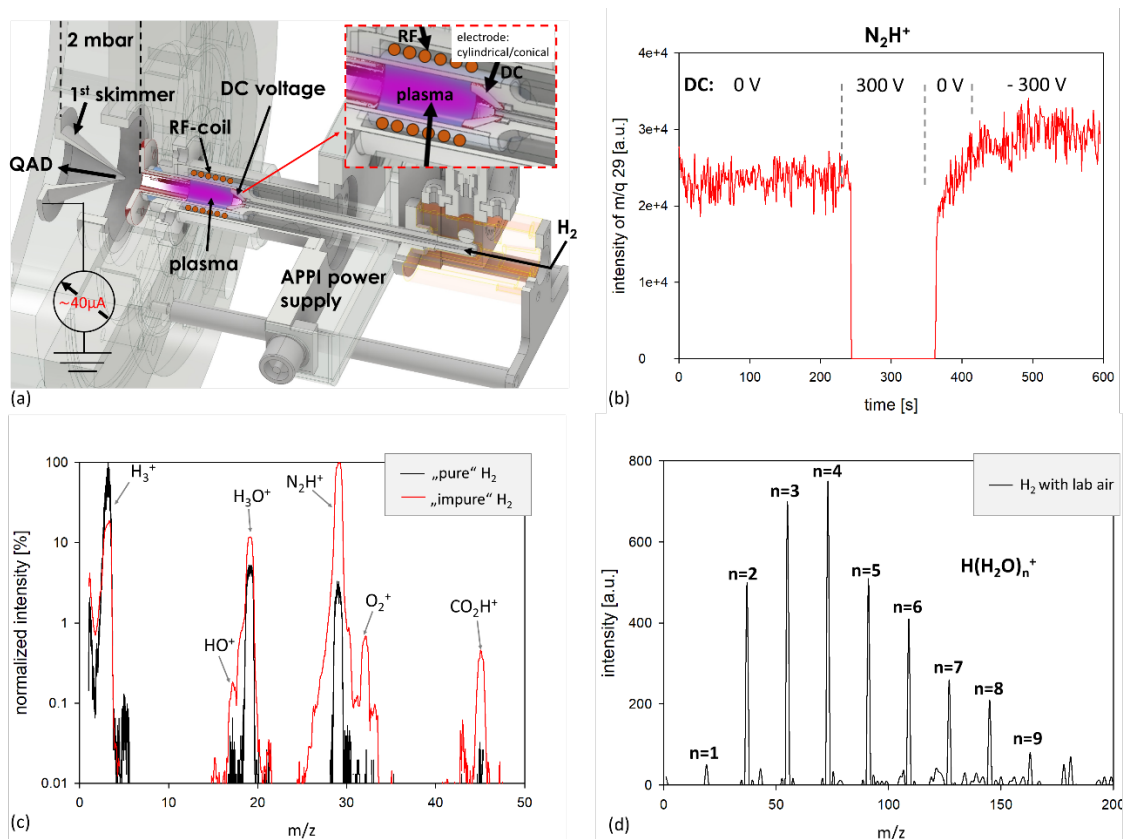


Figure 53 (picture and data from [159] and [146]): (a) Illustration of the hydrogen HR plasma in an open configuration interfaced with the Hiden HPR60 quadrupole mass spectrometer. (b) Data demonstrating the impact on the N_2H^+ current by an additionally applied DC voltage. (c) Mass spectra of the hydrogen HR-plasma and (d) mass spectrum of the hydrogen HR-plasma with addition of lab air.

A glass tube (type 8252, Schott AG, Mainz, Germany) with an outer diameter of 12 mm and an inner diameter of 10 mm was inserted into the first differential pressure stage of the MS. Hydrogen was introduced from the rear side with flows up to 20 sccm. A standard APPI power supply as used in conventional ion sources for mass spectrometers (cf. chapter 2) provided the required RF input. The pressure of the plasma gas was essentially the same as in the first differential pumping stage since no flow restriction was inserted in between. With an additional valve to the forepump, this pressure was adjusted within a range of $1 \cdot 10^{-3}$ mbar up to a few mbar, but was typically maintained at around 2 mbar throughout the experiments. The afterglow plasma zone was in line of sight with the first skimmer, located in roughly 1 cm distance. After the expansion, immediately behind the skimmer, the ion population is in a virtually collision free environment and then transferred further downstream to the quadrupole analyzer (QAD). An electrometer (610C, Keithley Instruments, Cleveland, OH, USA) connected to the first skimmer was

used to record total ion fluxes. Upstream of the plasma volume an additional DC voltage could be applied through either the plain cylindrical end of a metal capillary or a conically shaped electrode, as illustrated in the enlarged image in Figure 53(a).

The essential results from Mr Kutsch's work are summarized in Figure 53, which were also partially presented in two poster presentations at the 2017 ASMS in Indianapolis, IN, USA [145, 146]. First of all, the standard APPI RF power supply generates a stable and reproducibly ignitable open H₂ plasma between 1 and 5 mbar with flow rates between 1 and 20 sccm. A current of the order of 40 μ A, corresponding to 10¹⁴ singly charged ions per second, was recorded on the first skimmer. Owing to the line of sight with the plasma, these figures must be treated with some caution, since photoelectrons released from the metal surface may contribute to the overall current as well. Nevertheless, as a preliminary result this experimental value implies the generation of sufficient primary charge carriers to eventually operate a sensitive chemical ionization source.

Furthermore, additional DC voltages significantly impacted the RF plasma. Figure 53(b) illustrates how an additionally applied DC voltage on the cylindrical electrode version altered the species resolved ion current recorded with the MS. Shown is the intensity of m/z 29 corresponding to the protonated nitrogen N₂H⁺. At 0 V a constant signal was recorded, which instantaneously vanished with +300 V applied. The signal recovered relatively fast with a reset of the electrode voltage to 0 V. This eventually allowed to pulse the positive currents leaving the plasma zone with at least 1 Hz between zero and maximum intensity. Virtually no changes in intensity were observed with applied negative voltages up to -300 V. The exact same trends were obtained for all other mass signals, such as H₃⁺. Also the skimmer current was significantly modified by applying a positive DC voltage of 300 V to the cylindrical rear electrode [206]. At the switching point from 0 to +300 V the current turned from constant +40 μ A to a strongly fluctuating signal between +40 μ A and -145 μ A. Resetting the electrode to 0 V recovered the constant 40 μ A output instantaneously and no effect on the current was noticed between 0 V and -300 V, which is in accordance with the mass signal trend. Replacing the electrode with a conically shaped device (cf. Figure 53(a)) allowed to significantly alter the ion currents in a similar way, however, at strongly different DC values as compared to the cylindrical version. A floating electrode yielded an intense and constant H₃⁺ ion signal that immediately collapsed by four orders of magnitude when connected to ground potential. The signal did not recover in the range between -100 V and +300 V. Between +300 V and +1 000 V the H₃⁺ intensity levelled to approximately 20 % as compared to the floating condition. Between -100 V and -1 000 V the H₃⁺ intensity steadily increased and even exceeded the floating potential reference signal by a factor of 60. In all cases, positive DC values did not favor the direction of positive ions flowing from the RF plasma volume to the MS. Therefore, an effective DC gradient from the anode through the plasma to the grounded

skimmer is discarded. In this event, an increase of positive ions entering the MS would have been expected. Mr. Kutsch's findings, however, suggest the presence of sufficient charge density to effectively shield the additional electrical field. The results indicate a rather strong interference between the RF plasma sheath and the DC electrode surface. The substantially enhanced H_3^+ flux with negative voltages applied to the conical electrode could be interpreted in terms of a superimposed secondary amplification effect, as discussed for DC plasmas in chapter II, section 2.1.1.2. Increasing the potential drop between the plasma volume and the electrode accelerate positive ions across the sheath towards the electrode. The stronger the impact on the surface, the more secondary electrons are liberated and directed into the plasma by the respective gradient. When these additional electrons gain sufficient kinetic energy from the RF field, an overall increase of the plasma density is expected and leads to the observed 60-fold enhanced H_3^+ flux. It appears as if this explanation is also in accordance with the substantially different plasma behavior when using the two electrode shapes. The conical version offered a significantly larger surface for this amplification process to occur than the small tip of the metal capillary. Consequently, a negative DC voltage applied to the latter should have less effect on the positive ion flux, which was demonstrated in this work. These considerations on applying a superimposed DC gradient to the helical resonator RF plasma are purely qualitative and lack the precision of an applicable model. As stated in Mr. Kutsch's thesis outlook, a profound understanding of the underlying elementary principles and the practical potential of this operational mode require a more in-depth exploration. Specifically, we need to closely examine and analyze the alignment between the spectrally resolved emission and the ion fluxes. Such data could visualize the impact of an additional DC field on the anticipated changes in the electron energy distribution and the total plasma density. However, in the course of using the helical resonator plasma for CI applications this operational mode has not been further explored yet, since a completely electrodeless approach was favored.

In his thesis, Mr. Kutsch briefly touched on the susceptibility of the plasma ion chemistry to minor modifications of the neutral constituents. This turned out to be one of the key challenges in the research and development (R&D) for the commercial CI system (cf. section 4.2). The spectra depicted in Figure 53(c) for "pure" and "impure" H_2 conditions were recorded with hydrogen obtained from two different compressed gas cylinders, both with a stated purity of 99.999 %. The "pure" spectrum shows protonated hydrogen as the most abundant species, followed by protonated water and protonated nitrogen with relative intensities of 5 % and 3 %, respectively. Note the logarithmic scale for the y-axis. The more "impure" batch from the same gas supplier led to ion abundances in the following descending order: N_2H^+ (100 %), H_3^+ (18 %), H_3O^+ (12 %), O_2^+ (0.7 %) and CO_2H^+ (0.5 %). The spectrum in Figure 53(d) was recorded with addition of a minor flow

of laboratory air downstream of the plasma region, upstream of the aperture of the 1st skimmer. Under this condition all the species assigned in Figure 53(c) virtually vanished in favor of a pronounced proton-bound water cluster distribution containing up to nine water molecules. To better illustrate the progression, a linear y-axis was chosen. These preliminary results already indicated the delicate ion chemistry involved and pointed to the critical parameters to control. For an initial, qualitative treatment of these results we should have a closer look at the rate constants of ion-molecule reactions involved and the thermodynamic properties of some of the species listed in Table 3.

*Table 3: Proton affinity (PA) corresponds to the negative of the enthalpy and gas phase basicity (GB) to the negative of the Gibbs free energy of reaction for the protonation $M + H^+ \rightarrow MH^+$; ionization energy (IE) corresponds to the energy required for the vertical ionization process. **a** data taken from [41]; **b** data taken from [207].*

species	PA [eV] ^a	GB [eV] ^a	IE [eV] ^a	species	PA [eV] ^b
He	1.84	1.54	24.59	H ₂ O	7.16
Ar	3.83	3.59	15.76	(H ₂ O) ₂	8.72
O ₂	4.36	4.11	12.07	(H ₂ O) ₃	9.69
H ₂	4.38	4.09	15.43	(H ₂ O) ₄	10.43
N ₂	5.12	4.81	15.58	(H ₂ O) ₅	11.09
CO ₂	5.60	5.34	13.78	(H ₂ O) ₆	11.66
H ₂ O	7.16	6.84	12.62	(H ₂ O) ₇	12.16
C ₆ H ₆	7.77	7.52	9.24	(H ₂ O) ₈	12.61
NH ₃	8.84	8.48	10.07		

In a plasma with 100 % hydrogen, the formation of H₃⁺ is thermodynamically and kinetically favored under the given conditions of pressure and reaction time. Initial H⁺ requires a third collision partner to form H₃⁺ [208], whereas initial H₂⁺ ions react with neutral H₂ in a bimolecular process at a rate of 2·10⁻⁹ cm³·s⁻¹ to form H₃⁺ and an H atom [209]. In fact, the latter is faster than the collision rate calculated from simple gas kinetic theory, but due to long range, charge-induced dipole potentials, it is generally a common value for ion-molecule reactions [210]. “Most reactions are found to proceed at the collision rate or not at all” as aptly stated by Anicich in the introduction of his comprehensive compilation of bimolecular cation-molecule reaction rates [209]. Once a sufficiently large H₃⁺ population has built up, we find a useful starting point for a very versatile chemical ionization source based on proton transfer reactions. With a proton affinity (PA) of 4.38 eV, this ion is one of the strongest gas phase acids and readily protonates any molecule with a higher PA, such as N₂, CO₂ and H₂O with values of 5.12 eV, 5.60 eV and 7.16 eV, respectively (cf. Table 3). Again, these ion-molecule reactions proceed extremely fast with rate constants of the order of 10⁻⁹ cm³·s⁻¹. Therefore, even impurities in the ppbV range and a few collisions are sufficient to cause an ion-population distribution as observed for the “pure” hydrogen batch in Figure 53(c), where nitrogen and water both appear in their protonated form. In this context, a unique chemical system is found in H₂/N₂ plasmas. With the exception of N⁺, all cationic species in this mixture eventually

lead to the formation of N_2H^+ . If the latter is the preferred protonating reagent in the CI source, this system allows to directly sustain a hydrogen/nitrogen plasma with mixing ratios in the percent range, provided that the electron temperature is not too high for the formation of N^+ (the appearance energy of N^+ from N_2 is 24.3 eV [41]).

Figure 53(c) depicts a second spectrum from a more “impure” hydrogen plasma, showing a significant increase of the protonated water, nitrogen and also carbon dioxide population, which seems in reasonable agreement with the corresponding *PA* trend. A closer look at the appearance of O_2^+ is worth being taken. The proton affinity of oxygen is 0.02 eV below hydrogen, suggesting the absence of O_2H^+ , which is in accordance with the experimental data. This interpretation is not entirely correct though, since the proton affinity is a thermodynamic measure for the potential energy change involved in a chemical reaction. To indicate the direction, the entropy contribution has to be considered as well, which renders the gas phase basicity (*GB*), i.e., the negative of the Gibbs free energy, the more appropriate measure. However, in most protonation reactions the change in entropy is negligible as compared to the enthalpy change, hence in the literature the *PA* is often used as the only thermodynamic quantity, also for the direction in which the reaction proceeds. In case of oxygen and hydrogen, however, we find a minor difference in the *PA*s and the influence of the entropy change cannot be regarded as insignificant anymore. In fact, the entropy contribution favors the protonation of oxygen through H_3^+ by 0.02 eV (cf. *GB* in Table 3), which is also seen in the corresponding rate constants of $6 \cdot 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$ for the forward and $3 \cdot 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$ for the back reaction, respectively [209]. Thus, the absence of O_2H^+ is not reasoned by thermodynamic but kinetic arguments. The abundant presence of neutral H_2 , as compared to O_2 , easily overcompensates the factor of two difference in the respective rate constants and thus strongly favors the back reaction from O_2H^+ to protonate H_2 . Having clarified the “missing” protonated oxygen signal, the reaction channel for O_2^+ generation still requires some explanation. For H_3^+ , no charge-transfer path with subsequent dissociation into neutral H_2 and H is known, hence this cannot be the source of the observed oxygen radical cations. Consequently, the initial assumption of a primary H_3^+ population responsible for all further reactions cannot hold for the prevailing experimental conditions. Either all impurities were also partially ionized by energetic plasma electrons or by H_2^+ . The latter provides a charge transfer as well as a proton transfer path for each of the observed impurities, except for nitrogen due to its higher ionization energy (cf. Table 3). For O_2 we find a charge-transfer/protonation ratio with H_2^+ of 30:70, for H_2O and CO_2 50:50 and 30:70, respectively [211, 212]. Similar to N_2^+ , also CO_2^+ and H_2O^+ react rather fast with hydrogen transferring an H atom to the final protonated forms of each species, as observed in the experimental spectrum. Only O_2^+ , as discussed above, will remain in this state. Consequently, for a hydrogen based chemical ionization source with a well-defined

protonation scheme, the presence of oxygen in the plasma region should be avoided, since it provides a charge sink.

Another quite remarkable spectrum is shown in Figure 53(d), demonstrating the effect of adding a minor flow of laboratory air downstream of the plasma region. All previous plasma species virtually vanished in favor of a pronounced proton-bound water cluster distribution containing up to nine molecules. A glimpse at the *PAs* or *GBs* in Table 3 reveals that all the protonated species discussed above will protonate water. However, O_2^+ seems to be inert towards water since its ionization energy is around 0.6 eV below the *IE* of H_2O . How can we explain the disappearance of O_2^+ in favor of the observed cluster distribution? In 1969, Fehsenfeld and Ferguson postulated a mechanism for the observed water ion population in the D region of the earth's ionosphere starting with O_2^+ [213]. They assume that initially an $O_2^+(H_2O)$ cluster is formed, followed by a reaction with a second water molecule yielding H_3O^+ , O_2 and an OH radical. A further, not immediately obvious result is the extent of the cluster distribution. At room temperature a distribution with a maximum of five water molecules in the cluster is usually observed [207]. This finding with up to nine water molecules is explained by a subsequent adiabatic expansion through the 1st skimmer, significantly cooling the gas. As depicted in Table 3 the proton affinity increases with increasing cluster size and the range of amenable analytes readily decreases. As an example, the compounds C_6H_6 and NH_3 are only protonated by H^+H_2O and $H^+(H_2O)_2$. Hence, operating a CI source based on the present plasma configuration requires careful control of the water content of the used gases.

In summary, it is rather difficult to reveal the exact plasma chemistry and mechanisms from these preliminary experimental findings in Mr. Kutsch's bachelor thesis, but this was not the intention. These results clearly demonstrated that (i) the helical resonator driven hydrogen plasma provides a sufficiently high primary ion current to efficiently operate a CI source between 0.1 and 10 mbar, (ii) the charge flow can be rapidly switched on and off with a DC voltage, which can also significantly increase the primary current, (iii) already minor impurities and a few collisions drive a rich and complex ion-molecule chemistry that needs to be carefully controlled for a well-defined CI scheme. Particularly the water content in the system requires special attention.

4.2 Development of a Commercial GC-CI-TOF-MS

Between 2017 and 2023 the two PhD students Dr. Kai Kroll and Dr. Steffen Bräkling have successively worked on a hydrogen based CI source for a time-of-flight mass spectrometer, with the ion-chemistry initiated by a helical resonator plasma. This project was partially funded by the Tofwerk AG, Thun, Switzerland and the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant

agreement No 764991. The final CI source as integral part of a novel, fast switching GC-CI&EI-TOF-MS system was successfully launched by Tofwerk in 2023 [158]. The scientific output for this project comprise the two PhD theses [166, 167], three publications [137-139], seven poster presentations [152, 206, 214-218] and one oral presentation [155] presented on several international conferences. This chapter briefly highlights some key steps and findings related to the GC-CI-TOF-MS system, specifically focusing on the helical resonator device. The intricate details and specific methods used to quasi-simultaneously record and combine CI and EI spectra within the final GC-CI&EI-TOF-MS instrument are not discussed in this work. It is important to acknowledge though, that these aspects were primarily developed by Tofwerk AG and are thus covered by their intellectual property protections. For more details, the interested reader is referred to the above referenced publications, particularly to the two comprehensive PhD theses.

4.2.1 Short Historic Outline on Chemical Ionization

A short historic outline on CI will be given first, in order to contextualize our own approaches in this project.

As early as 1913 by the inventor of mass spectrometry himself, chemical ionization via a proton transfer reaction of the lightest molecule has been reported [219]. J.J. Thomson correctly assigned the signal at m/z 3 to the H_3^+ ion, however, erroneously interpreted his results as a newly discovered stable neutral H_3 species, always present to a certain extend in H_2 samples. Three years later, Dempster noticed a pronounced dependency of the relative distribution among H^+ , H_2^+ and H_3^+ on the H_2 ion source pressure. He finally explained his and also Thomson's findings as a result of a chemical ionization reaction path between a primarily generated H^+/H_2^+ population with abundant neutral H_2 to form H_3^+ [220]. Nearly half a century elapsed before the scientific benefits of using a mass spectrometer for ion molecule reaction studies was recognized, either for the determination of thermodynamic properties of molecules, such as the proton affinity [221] or for fundamental research of the upper partly ionized layers of our atmosphere on a laboratory scale [222]. Since then this field has exponentially evolved resulting in various experimental setups to elucidate fundamental molecular gas phase behavior of ions [223] and filling numerous thermodynamic [41] and kinetic databases [209] for a multitude of compounds. The analytical potential of chemical ionization, and more specifically protonation reactions as a "softer" alternative as compared to EI was first introduced by Munson and Field in 1966 [224]. In this context, the term "soft" implies less fragmentation and thus less mass peaks recorded per compound, ideally one signal unambiguously assigned in addition to the corresponding isotopic pattern. However, this "softness" strongly depends on the difference in proton affinities (ΔPA) between the

reagent gas and the molecule of interest. As mentioned in section 4.1, the PA value relates to the exothermicity of the protonation reaction and thus the amount of energy potentially available for the excitation of internal degrees of freedom. With considerable ΔPA for the proton transfer the analyte is prone to fragmentation. However, decreasing ΔPA by choosing a primary reagent with a higher proton affinity renders less compounds amenable to this particular CI method, as discussed along with the values listed in Table 3. Hence, any analytical application of chemical ionization invariably entails a balance between the extent of analyte fragmentation and selectivity, respectively. Munson and Field suggested methane as a suitable reagent gas. Ionized in a conventional EI-mass spectrometer with a slightly modified source volume of decreased gas flow conductance, this reagent forms several $C_xH_y^+$ species as reactant ions. At pressures of around 1 mbar, CH_5^+ and $C_2H_5^+$ are primarily responsible for subsequent protonation of compounds present in analytical quantities within the same volume. The PA s of the corresponding neutral reactants are 5.63 eV and 7.05 eV, respectively. For the lower mbar pressure range, this one-pot method with EI ionized methane has been the gold standard in analytical CI-MS for decades. In cases including rather “fragile” analytes, the PA of the reagent has been increased, e.g., by installing an additional NH_3 gas cylinder and generating NH_4^+ as the respective reactant ion (cf. Table 3). Over the years, a number of additional analytical CI-MS methods with alternative primary ionization means, operating pressure or reactant ion preparation have evolved. Many new names and abbreviations have been coined, some less scientifically sound but commercially more attractive. They all have in common the basic concept of mixing abundant primary ions with molecules present in analytical quantities and subsequently analyzing the reaction products with a mass spectrometer. The three most prominent methods in modern MS are APCI (Atmospheric Pressure Chemical Ionization), PTR³ (Proton Transfer Reaction) and SIFT (Selected Ion Flow Tube).

As the name suggests, APCI operates at high pressure with collision numbers of $10^9\ s^{-1}$. Under these conditions, nearly any reactive ion-molecule reaction system is driven into its thermodynamic equilibrium within a tenth of a millisecond. Hence, probing the evolution from the initial maximum chemical displacement to the equilibrated state is nearly impossible in APCI with common mass analyzers. This CI-system is generally *thermodynamically* controlled. From an analytical perspective the sensitivity of high PA analytes greatly benefits from the efficient titration of the reactant ions. For this reason, this method lacks the ability to accurately represent the relative neutral composition of two or more analytes with largely different proton affinities and largely different abundancies. Furthermore, in commercially available APCI sources the initial ion population is typically generated in a corona discharge in nitrogen with an unknown

³ A vast majority of the MS community confusingly uses “PTR” for only one certain type of proton transfer reaction, though semantically it clearly stands for the more generic term.

amount of water vapor present. As shown in Table 3, this rapidly leads to a certain proton bound water cluster distribution solely responsible for protonating the analytes, but without any means of control over the acidity and the respective selectivity or degree of fragmentation. The latter is less pronounced in some occasions due to improved dissipation of excess energy into the bulk gas as compared to low pressure conditions.

In classical PTR [225], water is used as the reagent as well, however, in a more controlled way. Typically, a hollow cathode discharge with water saturated gas generates the primary ion distribution at a few mbar of pressure. A subsequent reaction cell increases the effective ion temperature through more energetic collisions along an axially applied electrical field. This essentially drives the cluster equilibrium chemistry to solely H_3O^+ as the predominant reactant ion. Compounds in analytical quantities are added in the same cell and are protonated, provided the PA is higher as compared to water. Furthermore, the concentration of reactant ions is usually in large excess and the total number of collisions is kept low, which allows to treat the chemical system with a pseudo-first order kinetic approach. This *kinetically* controlled CI-method eventually allows for quantification, provided the first-order rate constants of protonation are available. A major drawback of PTR is the required electrical field with reduced field strength of at least 100 Td. As soon as an analyte molecule carries a charge through protonation, it is exposed to this drawing field as well and its ion temperature strongly increases. In this way substantial fragmentation of analytes due to collision induced dissociation (CID) has been observed, particularly in case of rather “fragile” compounds.

The final CI-method mentioned in this context is SIFT. It allows strict control over the type of reactant ions used and, similarly to PTR, the reactions with neutral trace compounds follow a first order kinetics. SIFT has evolved from fundamental ion-molecule reaction studies, e.g., for compounds present in the ionosphere of our planet and beyond. The principal setup for analytical applications uses a microwave-plasma in air to generate versatile reactant ions, followed by a quadrupole to filter the intended reactant ions and transfer them into a higher pressure reaction cell. Any ion type present in the plasma can be used for CI, either for protonation (H_3O^+) or for charge transfer (O_2^+ , NO^+ , etc.). This swiftly changeable selectivity is advantageous, since it facilitates additional identification through the characteristic ionization energies of analytes, in addition to the mass information. The elaborate hardware setup with an additional filtering quadrupole and the required pressure increase in the downstream path is a clear disadvantage. Moreover, it is not intended to alter the plasma chemistry to enhance or to specifically form one particular reactant ion type. Therefore, the number of protonating reagents available for CI is rather limited.

4.2.2 Principle Reaction System and Hardware Setup used in this Work

For the GC-CI-TOF-MS project we preferred a “consecutive” CI concept with spatially separated stages, as illustrated in Figure 54, reproduced from our 2022 paper [137]. This is in contrast to the one-pot reaction control in classical CI, which utilizes a constraint volume for generating the reagent ions *and* for the analyte protonation. In our approach, initially H_3^+ is formed by a helical resonator driven hydrogen plasma. In a second step these primary charge carriers can be converted quantitatively to reagents such as N_2H^+ , CO_2H^+ , $\text{H}^+(\text{H}_2\text{O})_n$ or NH_4^+ by adding the neutral precursor in sufficient amounts further downstream. Note that the number of possible reagents is not limited to these examples. Any compound with higher proton affinity than hydrogen can, in principal, be used. In the last step the analyte is added, protonated and finally transferred to the mass analyzer. This approach follows the general approach of flow-tube mass spectrometry [226]. It allows for most flexible selection of the protonating reagent type and thus most possible control of the final gas phase acidity the analyte encounters. It is pointed out that the optimum pressure for operating the plasma and for properly driving the ion chemistry complement each other rather well. Moreover, this regime between 1 mbar and approximately 10 mbar facilitates straightforward implementation into the first differential pumping stage of any API mass spectrometer or into any instrument designed for classical CI.

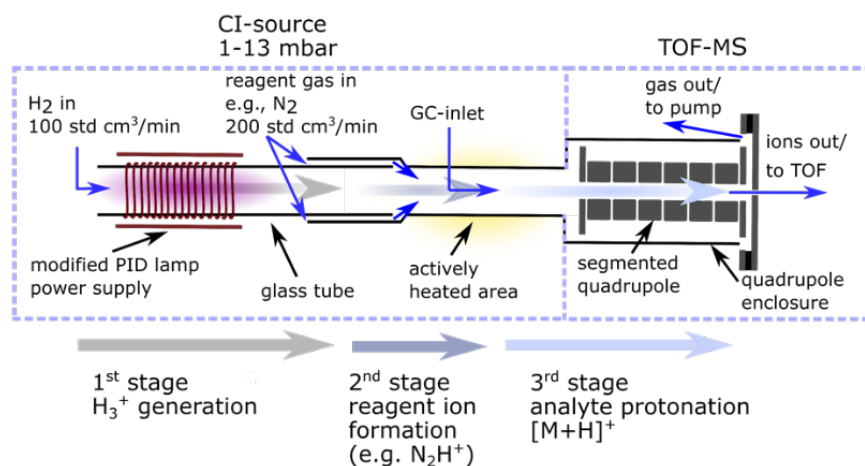


Figure 54 (adopted from [137]): Illustration of the consecutive CI concept with spatially separated stages.

In his PhD thesis, Dr. Kroll mastered technical issues to control and optimize the plasma and the synergistic ion-molecule chemistry of each stage. Figure 55 shows a chronological overview of the various setups constructed and employed. The schematic drawings are compiled from Dr. Kroll's PhD thesis [166].

For the first stage several modifications of the original PID helical resonator assembly were made to optimize the primary ion current. Foremost, the original RF coil was decoupled from the circuit board and replaced by a heat resistant (500°C) ceramic coated wire (KD 500 NPC, Karl Schupp AG, Zollikerberg, Switzerland) directly wound around the

plasma tube. With respect to GC applications, this enables heating of the entire source including the plasma region without affecting the electronic circuit. In addition to the Glass 8252 from Schott AG (Mainz, Germany) (cf. 3.4.1) also resistive glass (4.2 G Ω from PHOTONIS Inc., Sturbridge, MA, USA) was investigated as an alternative plasma tube material. The intention was to conceivably enhance the plasma ion extraction/generation in gas flow direction with an additionally applied axial DC field. Igniting and sustaining the RF plasma through the resistive material proved effective, with ion currents similar to previous experimental conditions. However, all delivered tubes lacked manufacturing tolerances with respect to roundness, causing severe sealing issues. For a low pressure CI source, which is highly sensitive to impurities, proper sealing is a key criterion. Consequently, this approach was not pursued further but should seriously be reconsidered with resistive glass tubes of proper physical dimensions.

For the second stage Dr. Kroll first implemented stacked chamber assemblies, with each compartment separated through orifices, as illustrated in Figure 55(a).

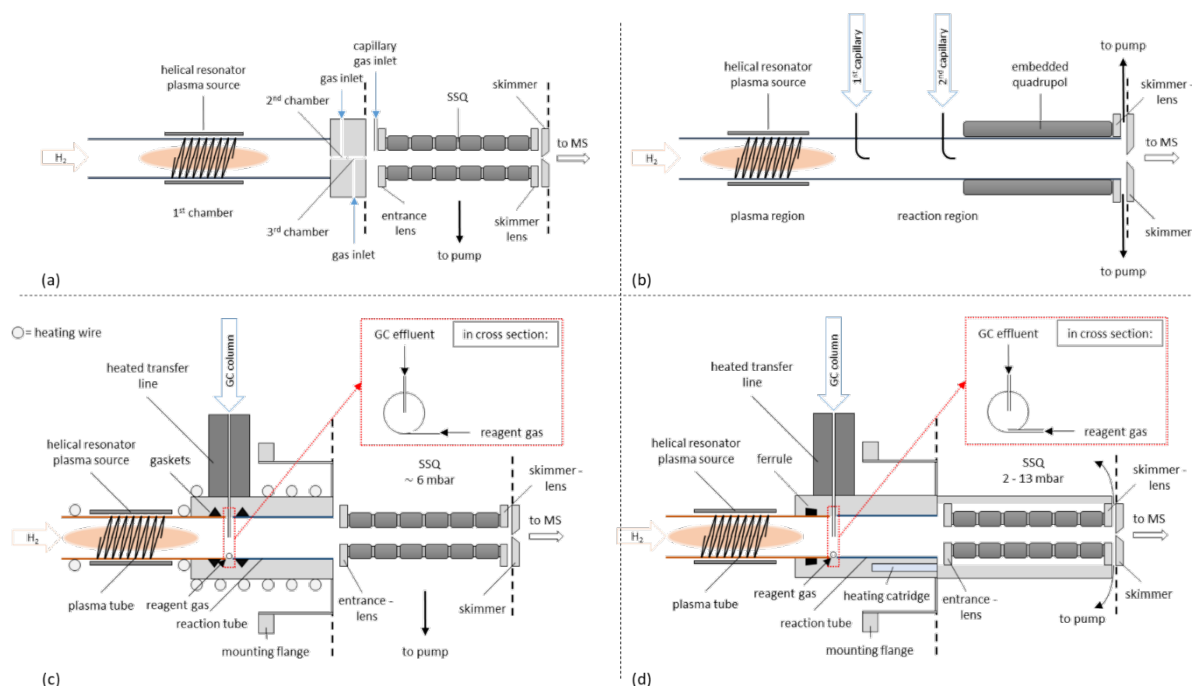


Figure 55 (adopted from [166]): Schematics of different CI designs built by Dr. Kroll.

The reason for the stacked chamber system was to spatially separate the ion-molecule chemistry into individual zones for optimal chemical control. This approach is adapted from Dr. Müller's PhD thesis [227] addressing high pressure, kinetically controlled plasma induced CI-sources⁴. However, it became evident that the constraint of small, consecutive

⁴ This project was under my supervision as well, but will not be subject of this writing. However, owing to Dr. Müller's work our group gained fundamental insight and experimental knowledge on handling ion-chemical systems. For more information in this regard, his thesis is highly recommended to the interested reader [227].

reaction volumes is in fact unnecessary for establishing a kinetically controlled ion chemistry under the prevailing pressures. Moreover, the separation orifices caused primary current losses of up-to two orders of magnitude, which made this approach less applicable. Therefore, subsequent iterations used continuous flow concepts for the reagent ion formation stage, as depicted in Figure 55(b)-(d). It should be noted though, that without any restriction, noticeable back diffusion of reagents into the plasma and direct photoionization through plasma radiation was observed. Additionally, there is a potential risk of increased analyte fragmentation due to incomplete conversion of H_3^+ to the final reagent ion population. Dr. Kroll carefully assessed these effects of which some will be discussed in section 4.2.3.

Analyte protonation and transfer to the next differential pumping region of the mass spectrometer occurs in the third stage. Dr. Kroll scrutinized several concepts for the inlet position of the analyte relative to the introduction of the reagent and for best possible reaction conditions. In the initial design (cf. Figure 55(a)), a continuous sample flow was introduced closely between the stacked chamber assembly and a “short segmented quadrupole” (SSQ), which was part of the original transfer unit of the TOF instrument. The second design (cf. Figure 55(b)) used more distant inlets for the reagent and analyte with both exits positioned on the center axis of the reaction tube. In the last two designs (cf. Figure 55(c)-(d)) the sample was again introduced at the center of the axis, while the reagent flow was tangentially aligned to the glass tube so that the laminar plasma effluent was radially surrounded. It became apparent that the relative position between those two inlets was not critical regarding the overall sensitivity of the system within the assessed range. Remarkably, however, the SSQ and its operational condition emerged as a key factor, not just for guiding and focusing ions, but most importantly, for enhancing the product yield in the final analyte protonation step. In his PhD work, Dr. Bräkling picked up and assessed this finding more closely. Reproduced from our 2022 paper [137], Figure 56(a) and (b) show results of the photoionization and protonation yield for xylene in dependence of the applied RF amplitude at different ionization source pressures.

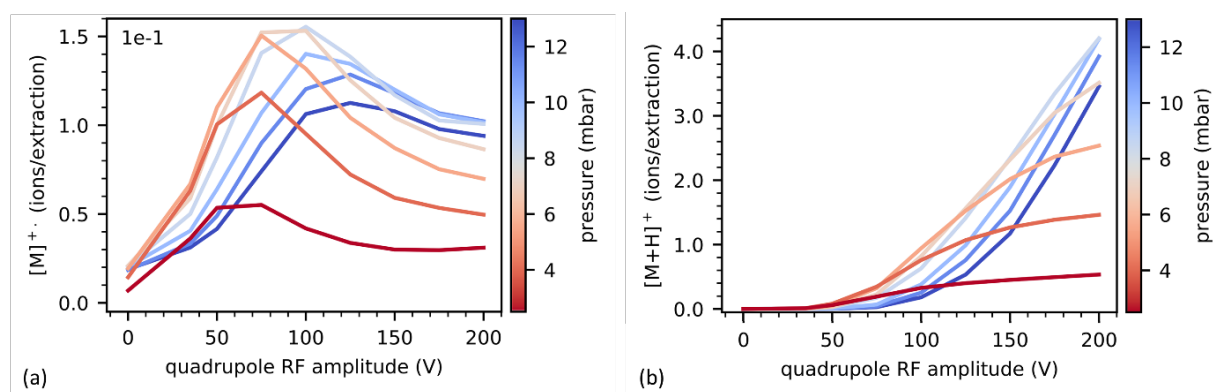


Figure 56 (adopted from [137]): Measurements of the (a) photoionization and (b) protonation yield for xylene in dependence of the applied quadrupole RF amplitude at different ionization source pressures.

The axial voltage gradient along the SSQ was kept below 10 V to avoid elevated reduced field strength and thus minimizing the extent of CID. The plasma glow is in line of sight with the third stage and causes a certain population of photoionized analyte molecules $[M]^+$ in addition to the protonated species $[M+H]^+$. This was generally observed with all analytes under investigation. From an analytical perspective, the photoion yield proved to be rather small if not negligible. However, the characteristic dependence of the abundance of each charged species on the SSQ RF amplitude revealed some insight into the complex superposition of transmission, diffusion, focusing and reaction dynamics. It seems reasonable that in case of the photoionized species only the transfer properties alter with varying RF amplitude. At all pressure settings the slopes of the $[M]^+$ intensity show a steep increase with a maximum transmission between approximately 80 V and 120 V. At higher voltages they level off to about 70 % of the maximum transmission. Even at 0 V $[M]^+$ ions were detected. We initially expected the $[M+H]^+$ progression to follow a similar trend. The experiment, however, revealed an additional effect of the applied RF field in the way ions and neutrals interact with each other. For the highest and the lowest pressure the $[M+H]^+$ signal was virtually absent at RF amplitudes below 80 V and 50 V, respectively. As reported in our paper [137]: "After the onset the signal increases exponentially and levels off for 2.5, 4, and 5.5 mbar at approximately 100, 150, and 180 V, respectively. The virtually parallel progression of all slopes suggests a plateau also for the higher-pressure settings at an extrapolated higher RF amplitude. A plateau indicates that the chemistry cannot be driven further by the quadrupole field. These significantly differing results between photoionization and protonation imply that the quadrupole not only affects the transfer properties, but also is an essential part of the third stage to further drive the chemistry of the protonation step (cf. Figure 54). It is assumed that efficient RF driven mixing of the reagent ions with the neutral analyte within the quadrupole field significantly amplifies the extent of ion-molecule-reactions. Additionally, the focusing effect concentrates reagent ions onto the quadrupole main axis, which leads to an increase in the rate of protonation. Figure 56(b) also shows an interesting pressure dependence of the observed $[M+H]^+$ population. For example, the plateau intensity for the four lowest pressures at 200 V exhibit a perfectly linear behavior. However, an interpretation is rather difficult since the pressure affects the plasma conditions, the reagent ion formation, diffusion, the protonation step and the transfer properties. To assess each contribution, further investigation is required. Nevertheless, the results allow to distinguish between transmission and chemistry effects and clearly demonstrate the importance of the quadrupole for the entire CI source design."

Dr. Kroll partially modeled and visualized the dynamics inside the SSQ with ion trajectory simulations. Figure 57 is reproduced from his thesis and illustrates the path of a N_2H^+ reagent population. Starting at the exit of the reaction tube on the left side, the initial

radial extent of approximately 8 mm is picked up by the entrance lens and rapidly focused to about 2 mm around the central axis within the first SSQ segment. This radial spread is maintained up to the skimmer lens, which finally narrows the ion beam to approximately 1 mm, matching the dimension of the subsequent skimmer aperture. It appears that a large fraction of protonation reactions take place around this central axis. A higher reagent ion density enhances the protonation rate, however, the neutral analyte is rather evenly distributed across the entire SSQ which minimizes the overlap. In addition, Dr. Kroll pointed out the considerable loss of ions at the entrance of the SSQ, due to the poor focusing property of the entrance lens, with losses approaching 80 %. Again citing from [166] “Any effort to focus the reaction tube gas flow into the SSQ by either restricting the reaction tube inner diameter with a nozzle end or the use of metal orifices, has shown significant ion losses on the surfaces. Focusing ions into the SSQ by means of electrostatic lenses is also very difficult at the given pressures, as suggested by respective simulations”. Consequently, in the continuing process of optimizing the instrument performance, Dr. Kroll correctly suggested the replacement of the SSQ by, e.g., an ion funnel system. Compared to quadrupoles, these devices offer significantly wider acceptance angles for ion beams and superior focusing capabilities, particularly for divergent beams within the relevant pressure range [228]. Such devices may also enhance the overlap between the neutral analyte and the reagent ion population. Further investigations and simulations in this regard are still pending.

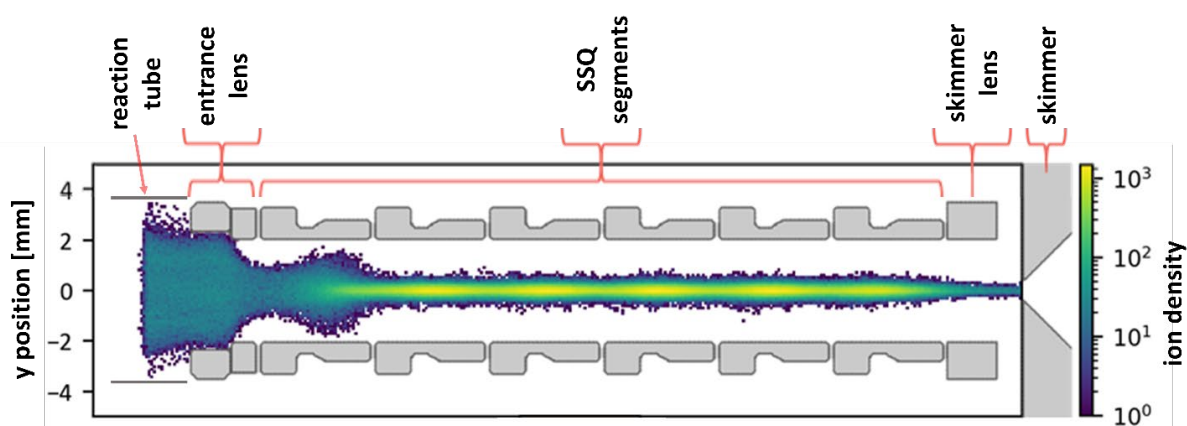


Figure 57 (adopted from [166]): Ion trajectory simulations of a N_2H^+ population inside the SSQ.

The GC-El&CI-TOF system received two further important hardware modifications regarding the CI source. These involved (i) enclosing the SSQ and (ii) implementing a technical solution for the GC effluent transfer [217] including the inlet to maintain distinct temperature zones: 300°C up to the inlet and room temperature at the TOF mounting flange. Figure 56(c)-(d) depicts some of these iterations. Dr. Kroll and Dr. Bräkling thoroughly assessed several heating concepts and sealing methods, resulting in excellent performance regarding constant gas proofness and outstanding chromatographic fidelity, also for high boiling compounds (cf. chapter 4.2.5). The SSQ enclosure was the final critical

optimization step for the chromatographic performance. Owing to a more confined, directed flow of the neutral analyte, this approach virtually eliminated previously observed peak-tailing issues.

4.2.3 Plasma Zone Effects

The plasma operates seamlessly with the downstream stages for reagent ion generation and analyte protonation, as shown in Figure 54. The proximity of the respective inlets to the active plasma region can cause unwanted side effects and add to the complexity of the recorded mass spectrum. While the visible plasma glow serves as a convenient indicator of the region containing fast electrons, it is important to bear in mind that high-energy photons and reactive species, in addition to the desired H_3^+ , can certainly penetrate much deeper into subsequent stages, extending well beyond this visible region. Additionally, back diffusion of neutral reagents and analytes into this zone can complicate analyses.

Dr. Kroll assessed some of these plasma zone effects by changing the distance of the helical resonator plasma along a glass tube, relative to an inlet for a 10 ppmV BTX - benzene, toluene and xylene mixture in nitrogen. The setup and some of the obtained results presented in Figure 58 are reproduced from [166]. The experiment utilized a hydrogen flow rate of 30 sccm through the plasma, while simultaneously introducing a BTX mixture at 100 sccm through the downstream inlet. The pressure within the system was maintained constant at 3 mbar.

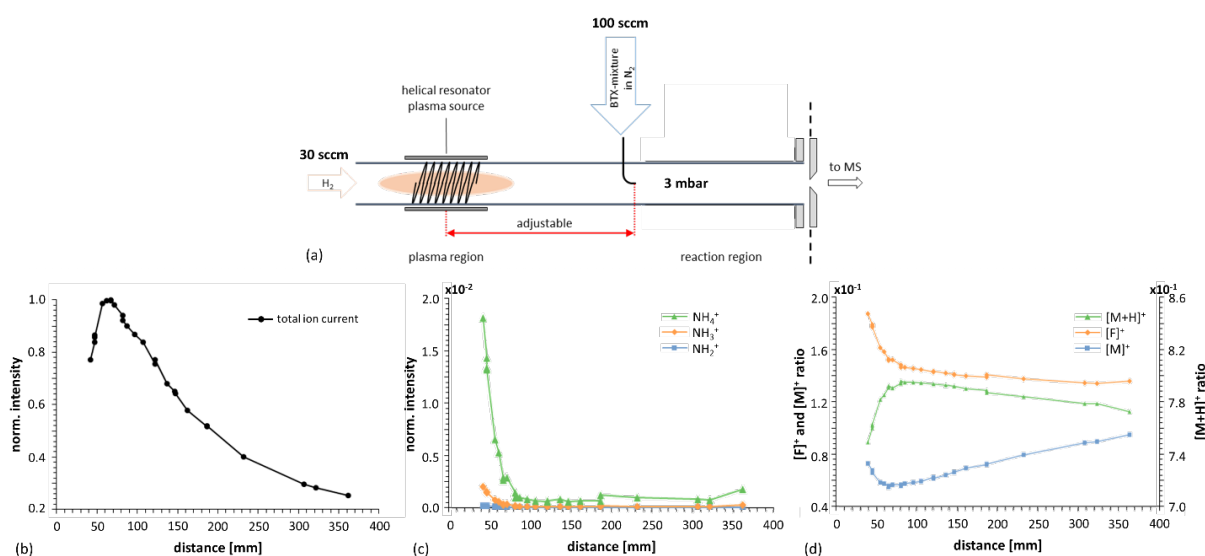


Figure 58 (adopted from [166]): (a) Schematic of the experimental setup for investigating plasma zone effects on the recorded mass spectra. Further shown are the effects upon varying the distance of the plasma relative to the inlet on (b) the total ion current, (c) the NH_x^+ formation and (d) the fragmentation, protonation and molecular ion formation of a 10 ppmV BTX mixture.

Each plot shows the varied distance between the center of the plasma and the downstream inlet in the range of 40 to 370 mm. Figure 58(b) depicts the expected

exponential decrease of the total ion current with increasing distance. Starting with the maximum intensity at 60 mm, an attenuation of 75 % is observed with an additional separation of 300 mm. This decline is mainly attributed to the progressive diffusional loss of ions on the glass surface. The signal decrease observed between 60 and 40 mm may initially appear unexpected. At this distance, the visible plasma region overlaps with the BTX inlet. An increase of both extent of fragmentation and formation of NH_x^+ species through the direct electron interaction occurs, which lead to a greater abundance of lower mass ions. The combination of this mass shift and the transfer quadrupole's low mass discrimination in the subsequent MS stage (not shown in Figure 58(a)) results in the recorded mass spectra underrepresenting the true total ion currents.

In general, we found the presence of NH_x^+ in a mass spectrum to be a valuable indicator for the proximity of the visible hydrogen plasma region to a downstream nitrogen inlet and for back diffusion effects. At the closest distance of 40 mm, the data show abundances relative to the total ion current of 2 %, 0.2 % and 0.1 % for NH_4^+ , NH_3^+ and NH_2^+ , respectively (cf. Figure 58(c)). In contrast to the total ion current, a considerably steeper drop in intensity of these species is observed within the first 50 mm of additional separation. This is readily rationalized, since the formation of NH_x^+ necessitates the dissociation of N_2 in the presence of plasma electrons with sufficient kinetic energy. This condition is only met within the boundaries of the plasma glow. Principally, two routes of NH_x^+ formation are conceivable, one starting with neutral and the other with singly charged nitrogen ions. The latter proceeds from N^+ in successive gas phase reactions with molecular hydrogen. Each step occurs close to collision rate up to NH_3^+ . The rate for the final step leading to NH_4^+ , however, is three orders of magnitude lower [209]. The initial neutral pathway is most likely a heterogeneous process on the glass surface: Primary N-radicals diffuse from the plasma volume to the surface and either react with molecular or atomic hydrogen in successive H-addition steps. The protonation via H_x^+ , followed by detachment and release into the gas phase is possible for each intermediate. From the presented data in Figure 58(c) and the prevailing plasma condition, two arguments clearly support the initial neutral pathway: (i) We observe a significant higher intensity of NH_4^+ as compared to NH_3^+ . As mentioned before, the rate for the last H-addition step is several orders of magnitude smaller. Therefore, in case of initial N^+ we would have expected a considerable higher $\text{NH}_3^+/\text{NH}_4^+$ ratio than observed. (ii) The energy required to dissociate N_2 into two neutral nitrogen atoms is 9.8 eV, as compared to 24 eV for the dissociation into N^+ and N [41]. As discussed before, for most low temperature plasmas, the ionization energy of the main gas approximately indicates the position of the prevailing electron kinetic energy distribution. Consequently, with an IE of 15.4 eV [41] for H_2 , not many electrons with 24 eV are expected to be present. This essentially excludes efficient production of NH_x^+ via the ionic pathway in the gas phase and renders the

neutral, heterogeneous mechanism with an initially required electron kinetic energy of 9.8 eV more favorable.

Dr. Kroll also investigated the extent of fragmentation and photoionization with altered plasma displacement. The yields of the respective BTX species are presented in Figure 58(d) in addition to the protonation yields. Each yield is normalized to the sum of all observed BTX related signals. The data clearly show that fragmentation starts to increase at overlaps below 80 mm distance between the plasma glow and the BTX inlet. Again, energetic electrons in this region are responsible for this effect, which is in line with elevated NH_x^+ formation (cf. Figure 58(c)). In the range of 100 to 370 mm, the fragmentation process shows minimal variation. This is attributed to the consistent protonation by the final reagent ion, N_2H^+ . The constant degree of fragmentation arises from the inherent differences in proton affinities between the BTX molecules and the N_2H^+ ions. These differences dictate the amount of excess energy available for fragmentation following the protonation event; employing a different reagent with a lower gas-phase acidity results in a reduced degree of fragmentation. This observation underscores the crucial role of the chosen reagent's proton affinity impacting on the extent of fragmentation observed in the experiment and will be discussed in section 4.2.4. As expected, the data in Figure 58(d) also show an inverse proportional relation between the extent of fragmentation and protonation. This trend is most pronounced in the region of overlapping distance with the plasma glow, specifically below 80 mm, where a reduction of 6 % is observed in the abundance of $[\text{M}+\text{H}]^+$. At 80 mm Dr. Kroll found a maximum protonation ratio of approximately 80 %, slightly decreasing with increasing separation up to 370 mm. This correlation is readily rationalized with a look at the exactly opposed trend of the molecular ion ratio in this region. It implies that the loss rate of reagent ions along the glass tube is higher than the loss of the VUV-photon flux for the same distance. Consequently, we find a steeper drop in $[\text{M}+\text{H}]^+$ formation with increasing distance than for $[\text{M}]^+$ formation. The absolute abundance of $[\text{M}+\text{H}]^+$ still prevails with approximately 78 % even at the largest separation measured. Interestingly, the $[\text{M}]^+$ progression exhibits a distinct minimum and with incipient plasma glow overlap the data show a further increase between 80 and 40 mm. It stands to reason that this is partially related to additional electron ionization in this region, in addition to photoionization. Benzene, toluene and xylene all have ionization energies (9.2, 8.8 and 8.6 eV, respectively) that are close to the energy previously discussed as needed for the N-radical formation in the plasma zone, i.e., 9.8 eV.

In summary, Dr. Kroll assessed the optimal working point for the position of the helical resonator plasma relative to an analyte and reagent gas inlet. For the further design of a commercial GC-CI source, a distance of about 100 mm represented a good compromise between maximizing the ion current and minimizing unwanted effects caused by the

plasma zone. This finding is only valid when pressure and gas flow rates remain constant. Under these operating conditions, the formation of NH_x^+ ions is negligible, the production of radical cations is minimized, and the likelihood of protonation reaches its highest level. In addition, Dr. Kroll employed sophisticated fluid dynamic simulations to examine the influence of back diffusion. These simulations demonstrated that upon reaching a distance of 100 mm between the reagent inlet and the plasma zone, the concentration of N_2 originating from the inlet decreases significantly into the ppbV range within the plasma zone.

4.2.4 Proton Source with Tunable Acidic Strength

A critical factor for cascaded, flow-based chemical ionization sources is the water content in both the plasma and the reagent gas. Unlike conventional PTR-MS, the present method explicitly forgoes employing electric fields, shifting the water cluster distribution through ion temperature control (see section 4.2.1). Such an alternative strategy, however, requires precise regulation of the water concentration in the system.

As illustrated in Figure 59(b), the desired reaction cascade begins with H_3^+ from the plasma, aiming for its quantitative conversion to N_2H^+ (reaction (12)) and the dimer N_4H^+ (reaction (15)).

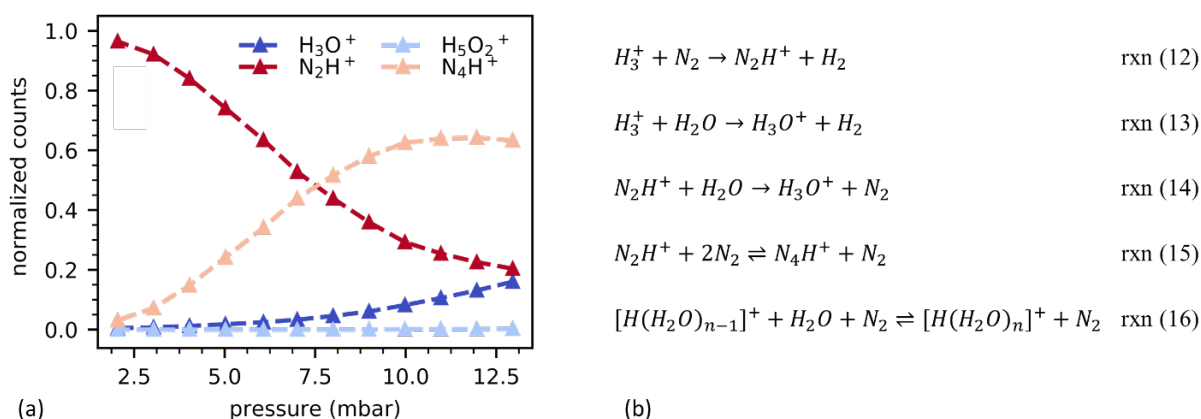


Figure 59 (adopted from [137]): (a) Measured reagent ion distribution with nitrogen and a water mixing ratio in the lower ppbV range in dependence of the pressure, starting the reaction cascade with H_3^+ , as shown in (b).

However, to best possibly exploit the advantageous acidity of protonated nitrogen species for subsequent reaction with analytes, it is pivotal to prevent the interaction with water according to reaction (12) and (14). This ultimately leads to an extended cluster distribution (reaction (16)) and inevitably lowers the overall reagent gas phase acidity. Therefore, to leverage the highest achievable acidity of the $\text{N}_2\text{H}^+/\text{N}_4\text{H}^+$ system, exceptionally high gas-phase purity is essential. Dr. Bräkling showed that a straightforward combination of hydrogen generator and a conventional purifier results

in an appreciable clean reagent ion distribution [137] with a water mixing ratio in the lower ppbV range. The plot in Figure 59(a) shows the characteristic pressure dependence of the reagent ion distribution of that particular system. Below 2.5 mbar virtually 100 % N_2H^+ was observed. With increasing pressure this monomer decreased in favor of the dimer with equal abundances at 7.5 mbar (reaction (15)). At approximately 13 mbar we found a nearly equilibrated system between the two protonated nitrogen species with approximately 20 % and 60 % relative abundances for the monomer and dimer, respectively. The H_3O^+ signal also constantly increased and constituted approximately 20 % of the remaining reagent ion spectrum at the highest pressure, while the proton bound water dimer $(\text{H}_5\text{O}_2)^+$ represented less than 1 %. Hence, even under these “pure” conditions, some protonated water was still present. At this point it was a question of balancing between more effort for even cleaner conditions and the practicability for the analytical end-user. We opted for the latter. The attained water concentration proved to be low enough to effectively suppress uncontrolled and extensive proton bound water cluster formation, thereby preserving an overall high gas-phase acidity within the reagent ion distribution. Furthermore, this initial condition presents a unique advantage: By meticulously controlling a gradual increase in the water vapor mixing ratio, the proton bound water cluster system can be strategically employed to achieve a well-defined, tunable decrease in the gas-phase acidity of the reagent ion distribution.

Complementing this CI approach, Dr. Bräkling developed a dedicated reagent gas supply unit. This design enables the precise addition of water vapor in the ppbV range, allowing for the controlled manipulation of the water cluster distribution. A schematic of the final setup, as reproduced from [139], is presented in Figure 60.

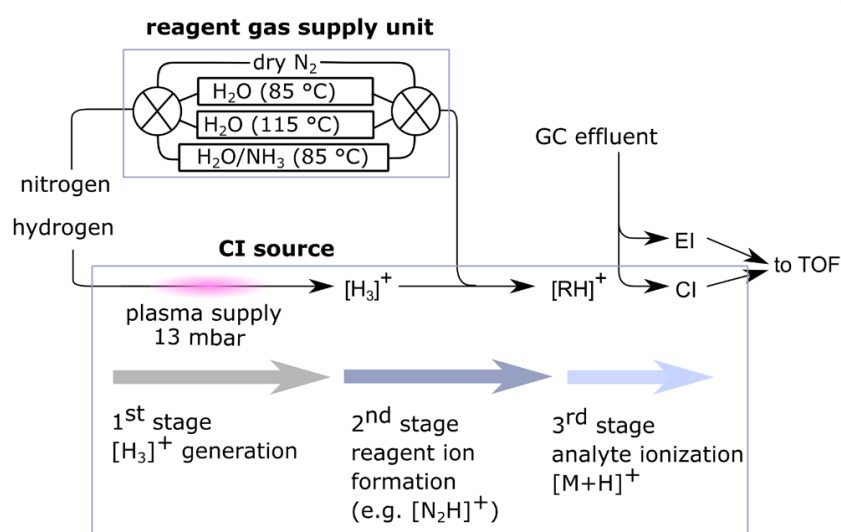


Figure 60 (adapted from [139]): Schematic of the developed reagent gas supply unit allowing for controlled manipulation of the water cluster distribution and rapid switching between predefined gas phase acidities.

Essentially, the reagent gas supply unit utilizes a temperature-controlled permeation tube system in which a main flow of nitrogen is enriched with dopants such as water or ammonia. High-purity water (Milli-Q®, 18 MΩ) is loaded into 10 cm long, ¼ inch OD Teflon® tubes with a 0.5 mm wall thickness. These tubes are capped with Teflon® rods and sealed using Swagelok® ferrules. An identical setup filled with a 30% NH₃/H₂O mixture is employed for the additional generation of ammonium ions, providing the lowest gas-phase acidity. The permeation rate of water and ammonia through Teflon® into the surrounding nitrogen sheath flow is highly temperature dependent. Therefore, the permeation tubes are housed within temperature-controlled, ½ inch stainless steel tubes. This configuration finally enables precise regulation of the reagent concentration introduced into the system by simply adjusting its temperature. As illustrated in Figure 60, three such heated assemblies are arranged in parallel to the nitrogen flow path. Two of these assemblies contain water, maintained at defined temperatures (85 °C and 115 °C) to achieve different permeation rates and thus two different predefined water gas-phase mixing ratios. The third assembly contains the NH₃/H₂O mixture. A fourth line is incorporated to supply pure and dry nitrogen for the highest possible reagent gas-phase acidity. To facilitate rapid switching between the various reagent sources, two 4-way valves are positioned on either side of the four stainless steel tubes.

The reagent ion mass spectra (RG1-4) in Figure 61(a)-(d) demonstrate the instrument's ability to swiftly switch between these four different predefined reagent ion distributions, each with a defined level of acidity. By analyzing the reaction rates of toluene and benzene with N₂H⁺ and H₃O⁺, Dr. Bräkling verified that these experimentally recorded distributions closely reflect the ratios of actively protonating species in the system [137]. In the step of analyte protonation, all reagent ions of such a distribution, each with their own specific proton affinity, are involved. To quantify the overall gas-phase acidity, we therefore use a signal intensity weighted mean $\overline{PA}$ value of the corresponding distribution with the standard deviation representing its width, rather than listing the *PA* value for each single reagent ion species. The proton affinities for (H₂O)_n, NH₃ and N₂ are taken from Table 3 as given in the referenced literature. For the ammonium dimer a *PA* of 9.4 eV was found in [229]. For the nitrogen dimer we used a *PA* of 5.4 eV, derived through our own ab-initio calculations (cf. section 5.1 in II SPARK PLASMA), since no other reported value was available. In this way the gas-phase acidity for the RG1 spectrum in Figure 61(a) with “dry” nitrogen was calculated as 5.7±0.8 eV. The protonated nitrogen dimer is the most prevalent species observed. The relative abundances of the protonated nitrogen monomer and the water signal are nearly identical, each constituting approximately 35 % of the intensity of the N₄H⁺ peak. Adding water vapor to the dry nitrogen flow using the H₂O filled permeation tube, which is maintained at 85 °C, results in the reagent ion distribution RG2 shown in Figure 61(b). The most abundant species is H₃O⁺, followed by

35 % for the proton bound water dimer and then the protonated nitrogen monomer and dimer with approximately 30 % relative intensity each. For the predefined RG2 a mean proton affinity of 6.9 ± 1.2 eV is derived.

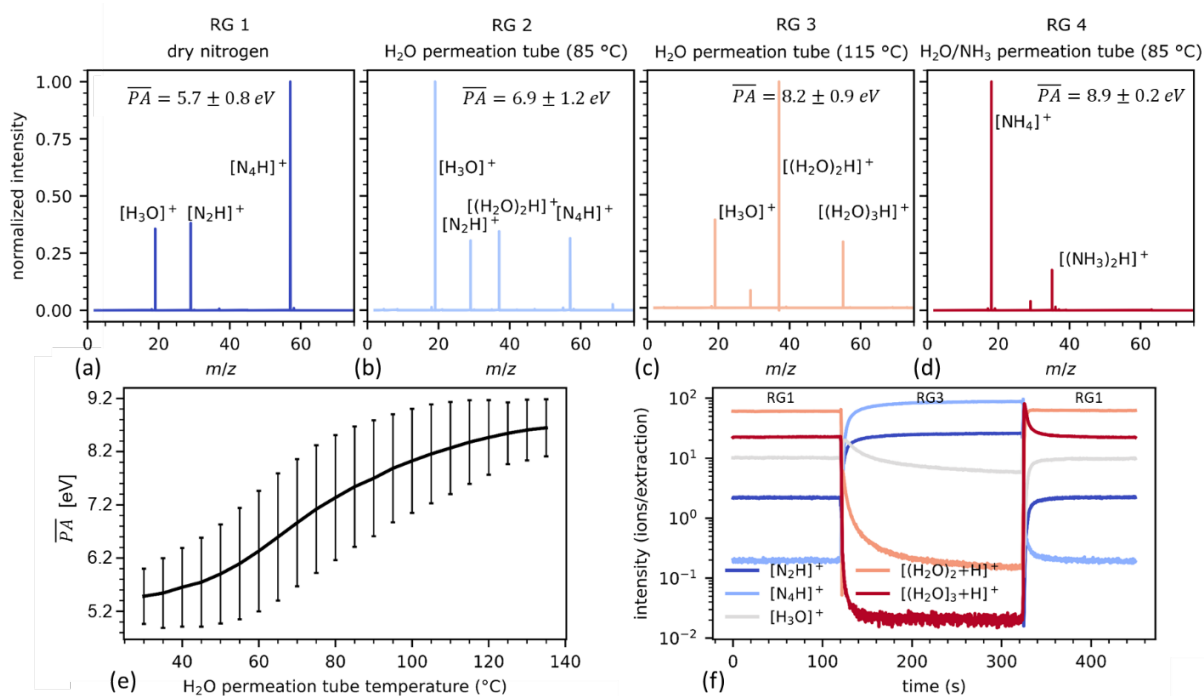


Figure 61 (adapted from [139]): (a)-(d) Mass spectra depicting how the new reagent gas supply unit affects the distribution of reagent ions for various pre-selected levels of gas phase acidity. (e) Plot showing the average gas phase acidity in dependence of the temperature as determined by analyzing the measured proton bound water cluster distributions at various permeation tube temperatures. (f) Temporal evolution of the reagent ions between two switching cycles from RG1 to RG3 and vice versa.

Increasing the permeation tube temperature to 115 °C adds sufficient water vapor to the nitrogen flow to quantitatively titrate the protonated nitrogen species, as shown for the predefined setting of RG3 in Figure 61(c). This mass spectrum is dominated by proton bound water clusters with the dimer being the most prevalent species. The relative intensities of the monomer and trimer are 40 % and 30 % relative to the dimer intensity, respectively. The 30 °C temperature difference between RG2 and RG3 causes a shift in the mean proton affinity of 1.3 eV with a derived $\overline{PA}$ of 8.2 ± 0.9 eV for RG3. Introducing ammonia into the dry nitrogen flow at 85 °C through the respective permeation tube quantitatively converts all available charges into protonated ammonium monomers and proton bound dimers. This is evident in the mass spectrum of reagent ion distribution RG4, shown in Figure 61(d), where NH_4^+ is the most abundant species and $(\text{NH}_3)_2\text{H}^+$ is present at approximately 20 % relative intensity. The corresponding weighted mean proton affinity for RG4 is 8.9 ± 0.2 eV.

These four pre-defined gas-phase acidities are not fixed, in contrast, this system offers the user extended control over the experimental conditions. By adjusting the temperature of the water-filled permeation tubes, the permeation rate of water vapor into the dry

nitrogen flow can be precisely tuned, effectively changing the resulting reagent ion distribution and its associated acidity. Figure 61(e) illustrates this concept. It presents a temperature curve alongside the resulting weighted mean proton affinities derived from the respective water cluster distributions. The standard deviation of the width associated with these proton affinities is also included, providing a comprehensive picture of the relationship between temperature, proton bound water cluster composition, and the overall gas-phase acidity. Dr. Bräkling investigated a temperature range from 30 °C to 135 °C. The average gas-phase proton affinity of the reagent ions exhibits a gradual increase, beginning at 5.7 eV and asymptotically approaching a maximum value of 8.7 eV, as the limit for this proton bound water cluster system.

From a practical standpoint, it was also worth taking a closer look at the switching behavior between different reagent tubes with regard to reproducibility of the reagent ion distributions and their respective equilibration times. Figure 61(f) shows the temporal evolution of the reagent ion populations between two switching cycles from RG1 to RG3 and vice versa. First of all the stability and reproducibility of the signals is excellent. Comparing the initial region of RG1 up to 100 s and the second region of RG1 starting at 340 s clearly demonstrates that the exact same distributions for dry nitrogen are obtained. No carryover of water vapor is observed in the system, although RG3 was used in between with an H₂O mixing ratio sufficient to completely deplete the protonated nitrogen species in favor of the expected cluster distribution, reflecting the mass spectrum of Figure 61(c). With regard to practical switching times we observe that after changing the reagent, an equilibration to the new distribution within 180 s is sufficient. Considering this system as part of a GC-MS, this time lies within a typical GC-cool down cycle. Hence, this approach allows for consecutive GC-runs with different gas phase acidities to fully exploit the analytical power of this system.

In summary, Dr. Bräkling successfully finalized the H₃⁺ plasma based chemical ionization source for this GC-CI-TOF-MS project. This system offers a versatile range of reagent gas-phase acidities, spanning from 5.7 eV to 8.9 eV. Protonated nitrogen acts as the strongest acid, while protonated ammonia is used as the weakest. This hydrogen plasma based approach is the only route to generate N₂H⁺ ions. Furthermore, we achieved precise control over the proton bound water cluster composition within the source. This was accomplished by initially using an ultra-pure plasma gas supply. Subsequently, a permeation tube setup was employed to meticulously introduce water vapor, allowing to deliberately shift the water cluster distribution towards a desired weighted mean proton affinity in a controlled manner. This strategy enables fine-tuning of the applied reagent acidity. While additional CI reagents, as for example methane and isobutane, were explored with the H₃⁺ source as well, in the final setup we settled on nitrogen, water, and ammonia. Readers interested in the results for other reagents, in particular the reagent

ion mass spectra of methane and isobutane are referred to our publication from 2022 [137] and Dr. Kroll's thesis [166].

4.2.5 Analytical Performance

The analytical performance of a GC-CI-MS system is usually evaluated using a number of key criteria. These include: Selectivity, sensitivity, detection limits, linear range, reproducibility, long-term stability, clear identification of the parent compound mass, degree of fragmentation, range of amenable compounds, peak shapes and tailing in particular for high boiling compounds. Dr. Bräkling carefully assessed these parameters for the introduced hydrogen plasma based CI source, of which some will be briefly presented in the following.

As discussed in the short historic outline on chemical ionization (section 4.2.1), the goal is recording a “clean” compound spectrum with ideally only the protonated species and its isotopic pattern present. However, chemical processes often deviate from this ideal behavior. For reaching an optimum proton transfer efficiency, the selection of the reagent's acidity needs to be balanced between a preferably broad coverage of PAs and minimizing the amount of excess energy to prevent fragmentation. Figure 62 depicts three total ion chromatograms of 2.5 ng injections of the standard EPA 8270 LCS mix, reproduced from [137]. This mixture encompasses 78 compounds representing a diverse range of chemical classes.

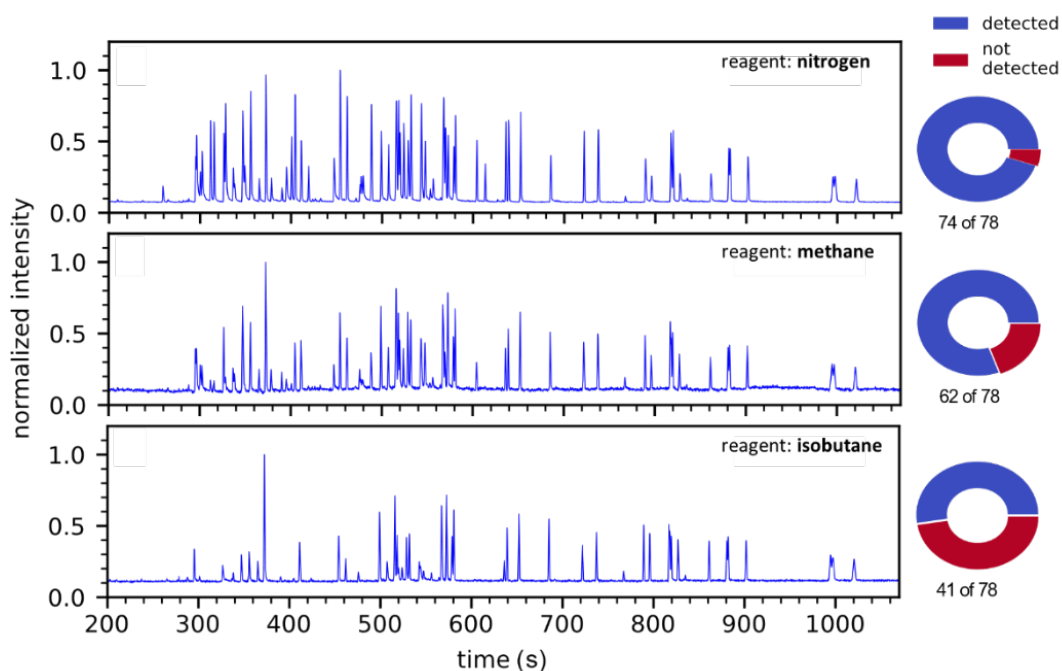


Figure 62(adopted from [137]): Three total ion chromatograms of 2.5 ng injections of the standard EPA 8270 LCS mix with the reagents (i) nitrogen, (ii) methane and (iii) isobutane in increasing order of their corresponding gas phase acidity. The diagrams depict the number of detected compounds with each reagent.

To demonstrate the impact of the reagent's acidity on the selectivity and fragmentation, the CI reagents nitrogen, methane and isobutane were introduced downstream of the hydrogen plasma. For nitrogen we observed the highest recovery with 74 out of 78 detected compounds. With methane and isobutane only 62 and 41 compounds were amenable to this method, respectively. This experiment nicely demonstrates the large compound discrimination, which translates to increased selectivity, upon lowering the gas-phase acidity of the reagent in the order: $PA_{\text{nitrogen}} < PA_{\text{methane}} < PA_{\text{isobutane}}$. In particular for non-target analysis of complex samples, this is a critical issue. A detailed list of the compounds in the EPA 8270 LCS mix and the observed base peaks with each reagent are available in the supporting information of our 2022 publication [137].

Figure 63 depicts a spectrum of benzophenone, an exemplarily selected compound, obtained with each reagent.

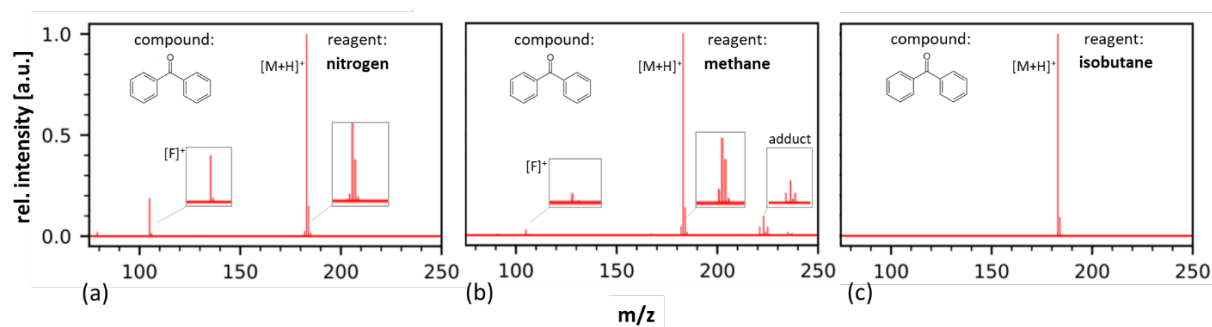


Figure 63 (adopted from [137]): Mass spectra of benzophenone acquired with (a) nitrogen, (b) methane and (c) isobutane as the reagent.

As expected, the extent of fragmentation $[F]^+$ decreases as upon switching from nitrogen (19 %), methane (5 %) and finally isobutane (0 %). This trend is in accord with the decreasing excess energies of 4.0 eV, 3.5 eV and 2.1 eV. These values are derived from the PA of 9.1 eV for benzophenone and 5.1 eV, 5.6 eV and 7.0 eV for the neutrals of the protonating species N_2H^+ , CH_5^+ and $C_4H_{11}^+$, respectively [41]. It is pointed out that the weighted average $\overline{PA}$ s were not considered, thus slightly lower excess energies are expected. For methane specifically, our experiments showed a wide distribution of reagent ions when interacting with the hydrogen plasma [137]. This suggests a larger deviation from the calculated excess energy for methane compared to the other reagents. This broad distribution also hints at a more complex ion chemistry operating, which is further supported by a pronounced adduct formation with compounds (cf. Figure 63). Along this line we also found more abundant $[M-H]^+$ formation using methane instead of nitrogen. Generally, the compound mass spectra appeared cleaner with nitrogen than with methane as the reagent, even though nitrogen is the stronger gas-phase acid.

Building on the work described in section 4.2.4 on the tunable proton source with the three reagents nitrogen, water and ammonia (cf. Figure 61), we further explored its analytical performance with the described preset gas-phase acidities [139]. This study

employed the final GC-CI&EI-TOF-MS for a non-targeted analysis of an artificial leather sample investigating the unknown, intricate mixture of volatile organic compounds it emits. The consecutive GC-runs of the same sample in Figure 64(a) illustrate the selectivity and amenable compound range for each preset gas-phase acidity, while Figure 64(b) depicts the implications on the fragmentation behavior of rather fragile compound classes.

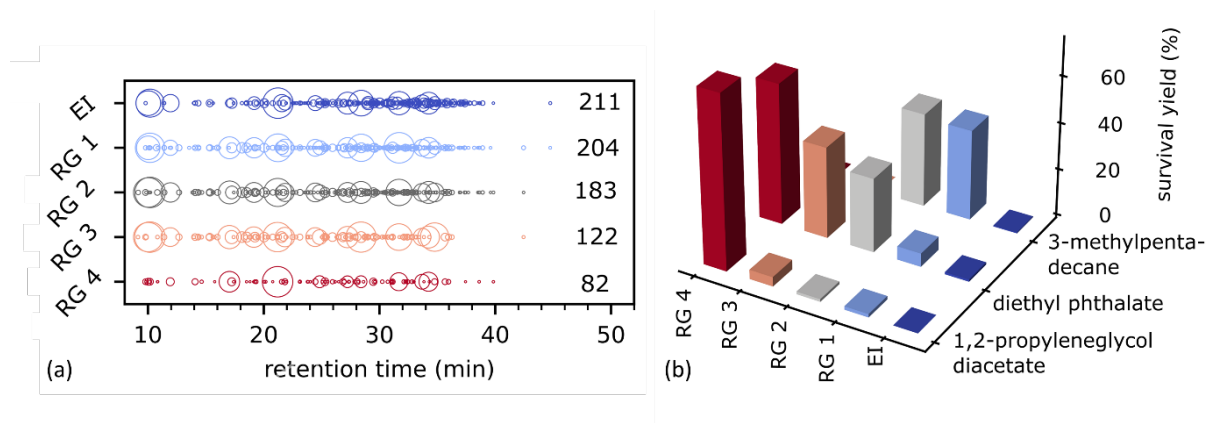


Figure 64 (adapted from [139]): (a) Illustrates the selectivity and amenable compound range for each preset gas-phase acidity and (b) depicts their implications on the fragmentation behavior of very fragile compound classes.

Again, dry nitrogen (RG1) proved to be a highly efficient reagent. It enabled us to detect 204 (97 %) out of the total 211 compounds identified using electron ionization as the non-selective reference method. The size of each marker in the figure reflects the relative intensity of the corresponding total ion current. Consecutively decreasing the acidity employing RG2 to RG4 decreased the number of detected compounds to 183 (87 %), 122 (58 %), and 82 (39 %), respectively, as expected. The large difference in selectivity between dry nitrogen and water-doped nitrogen or ammonia for this sample is readily attributable to the unique ionization efficiency of the N_2H^+/N_4H^+ ions. These ions effectively target alkanes, a prominent class of compounds found in this leather emission profile. In contrast, NH_4^+ ions do not protonate alkanes at all, and H_3O^+ and $(H_2O)_2H^+$ ions only achieve partial protonation.

Figure 64(b) focuses on three compound classes from the leather emission sample which are particularly fragile upon ionization. These are non-polar alkanes, phthalates and molecules with acetic groups, represented by the exemplarily chosen compounds 3-methylpentadecane, diethyl-phthalate and 1,2-propyleneglycoldiacetate, respectively. Regarding the corresponding mass spectra the interested reader is referred to the supplementary information in [139]. The extent of fragmentation is quantified by the *survival yield*. This figure refers to the relative abundance of a specific mass signal that unequivocally contains the sum formula information for the compound of interest. In case of electron ionization this essential information is completely lost for all three

compounds, which renders their identification based on EI impossible.⁵ Alkanes, as 3-methylpentadecane, benefit from efficient protonation with the $\text{N}_2\text{H}^+/\text{N}_4\text{H}^+$ system in RG1. This translates to a good survival yield of 38 % for the $[\text{M}-\text{H}]^+$, indicating that a significant portion of the molecules retain their structure after losing a hydrogen during ionization. For non-functionalized alkanes the $[\text{M}-\text{H}]^+$ commonly represents the main species in protonation reactions [230]. Adding water vapor to the reagent gas (RG2) provides a small enhancement of the survival yield of the $[\text{M}-\text{H}]^+$ ion for 3-methylpentadecane, reaching 40 %. However, there is a trade-off: The absolute number of all compound ions produced decreases. This effect becomes even more significant with RG3 - providing larger proton bound water clusters - and RG4 - the ammonia-enriched gas phase. In these cases, protonating 3-methylpentadecane becomes energetically impossible, and no signal is detected from this compound. The second compound class we studied is phthalates, with diethyl phthalate as a common example found in material emissions. Phthalates typically produce a characteristic and dominant fragment ion at m/z 149.0233 ($\text{C}_8\text{H}_5\text{O}_3^+$). This fragment is usually the strongest peak (base peak) in most phthalate mass spectra obtained with electron ionization at 70 eV, and it does not provide any information about the original molecule. This is also the case for diethyl phthalate. In contrast, with all CI reagents used, we identified the intact, protonated molecule of diethyl phthalate. As the average gas-phase acidity of the reagents gradually decreases, the survival yield of the $[\text{M}+\text{H}]^+$ correspondingly rises: 6 %, 31 %, 39 %, and 60 % for RG1, RG2, RG3, and RG4, respectively. The absolute abundances produced with phthalates are almost independent of the selected reagent gas. This is in stark contrast to what we observed with alkanes previously. Finally, the $\text{NH}_4^+ / (\text{NH}_3)_2\text{H}^+$ system used in RG4 is the most selective reagent, but it is also known for its gentle ionization behavior [231]. This was particularly noticed for the third compound class under consideration of acetic groups, which tend to fragment easily during ionization. A good example is 1,2-propylene glycol diacetate. Applying the protonated water cluster system (RG3), only 4 % of this compound remains intact upon protonation. Ammonia (RG4), however, promotes the formation of a stable and characteristic adduct for this class. In the case of 1,2-propylene glycol diacetate, an impressive 75 % yield of the adduct ion was observed. The chromatographic performance, sensitivity and detection limits are illustrated in Figure 65. In (a) chromatographic peaks of multiple 100 pg benzophenone injections recorded over a period of 6 days are shown. Each day represents an average of three injections with dry nitrogen (RG1) employed as the reagent.

⁵ This project on the development of a mass spectrometric tandem approach in collaboration with ToFwerk, is specifically motivated by this need. This novel method seeks to simultaneously acquire both EI and CI data within a single GC-chromatogram. For a detailed guide on leveraging the combined power of EI and CI data, high-resolution mass spectra, retention times, and characteristic fragmentation patterns for the identification of unknown compounds, we recommend referring to our publication [139].

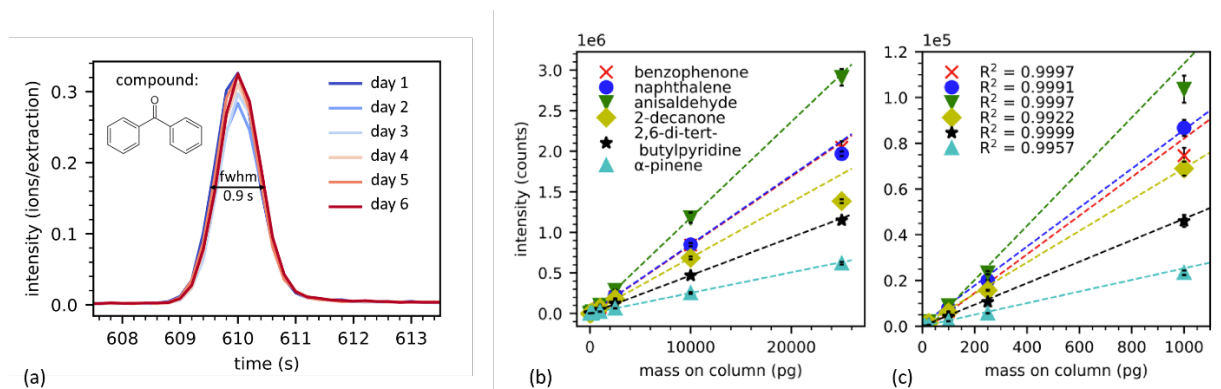


Figure 65 (adopted from [137]): (a) Chromatographic peaks of multiple 100 pg benzophenone injections recorded over a period of 6 days. Figure (b) and (c) display the linear range for the compounds benzophenone, naphthalene, anisaldehyde, 2-decanone, 2,6-di-tert-butylpyridine, and α -pinene in two different ranges for better visualization.

The recorded peak areas are in excellent agreement, signifying exceptional reproducibility and stability of the hydrogen plasma source and its subsequent CI stage. Furthermore, the peak shape is ideally Gaussian, devoid of any tailing or fronting, with a narrow fwhm of 0.9 s. These findings demonstrate the source's capability to maintain excellent chromatographic fidelity.

Figure 65(b) and (c) illustrate the linear range for six selected compounds: benzophenone, naphthalene, anisaldehyde, 2-decanone, 2,6-di-tert-butylpyridine, and α -pinene. Figure (b) displays the linearity range up to 25 000 pg injected mass on column. For better visualization of the lower range, Figure (c) presents an expanded view up to 1000 pg. Dry nitrogen (RG1) was employed as the carrier gas, consistent with Figure 61(a). The data demonstrate a linear range exceeding four orders of magnitude with R^2 -values >0.99 . This observation proves that the H_2 -plasma source driven by the helical resonator delivers stable ion currents and generates sufficiently high currents to prevent compound saturation effects with commonly encountered injected amounts in routine GC operation. Our analysis yielded limits of detection ranging from 0.4 to 1.2 pg on column. These values surpass published LODs for the same compounds analyzed using alternative GC-CI sources, such as a corona-plasma based approach [232].

In conclusion, the GC-CI source we developed, utilizing a medium pressure helical resonator-driven H_2 -plasma, demonstrated exceptional analytical performance. Its remarkable long-term stability ensures highly reproducible results. The source fully preserves chromatographic fidelity, as evidenced by exceptionally small peak widths and shapes. Furthermore, the switchable reagent acidity represents a significant advantage for enhanced compound identification. This approach complements the information obtained from high-resolution mass spectrometry, EI fragmentation patterns, and GC retention times. Dry nitrogen, with its associated protonating species N_2H^+/N_4H^+ , emerged as a particularly powerful reagent. It facilitates outstanding compound recovery

in complex samples while maintaining relative clean spectra, enabling unequivocal determination of molecular formulas. The achieved LODs fall within the lower picogram range, and the impressive linear range spans over four orders of magnitude.

5 Conclusion and Outlook

This chapter has highlighted the exceptional versatility of the helical resonator as a plasma source across multiple projects. Targeted modifications of a specific power supply based on APPI RF drivers have enabled this simple and cost-effective plasma source to be employed as: (i) A radiation source with ample *VUV photon flux* for the development of a GC-**PI**-MS setup and (ii) as a proton source providing ample of primary *ion currents* for the development of a GC-**CI**-MS setup.

In both fields the employed helical resonator displayed excellent performance across a wide pressure range, functioning effectively between 0.1 and 20 mbar. It exhibited exceptional long-term stability and consistent performance under largely different conditions. Even high-temperature operation, a necessity for interface to gas chromatography, presented no obstacles. This paved the way for seamless integration with existing GC workflows. Furthermore, a collaborative effort with Thermo-Fisher Scientific and MasCom GmbH successfully resulted in a GC-PI-MS system specifically designed for the Orbitrap high-resolution mass spectrometry platform.

In another project, a collaboration with Tofwerk AG further validated the successful application of a helical resonator-generated hydrogen plasma as a propellant for a chemical ionization source in mass spectrometry. This project received additional substantial funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement 764991. Both the GC-PI-MS system as well as the technology demonstrated in this collaboration were ultimately transitioned to successful commercial products.

To explore the full potential of this plasma type, several further projects investigated its fundamental properties. These projects revealed promising avenues for further research and diverse applications. One such example involves coupling the helical resonator to a conventional electron ionization triple quadrupole mass spectrometer. Initiated by research within a master's thesis [165], this route is pursued in an ongoing PhD thesis [169]. The primary focus of this research is the detection of volatile, highly oxygenated compounds, particularly relevant for atmospheric analysis.

Since May 2023, we are involved in the EU project 14AMI, supported by the Chips Joint Undertaking and its members, including additional funding from the BMBF (16MEE0370). Building upon our previous work, the helical resonator has been successfully adapted to

a gas phase sampling stage for extreme ultraviolet (EUV) lithography scanners. The patent application is currently drafted and will be filed soon.

IV LASER PLASMA

1 Abstract

In 2016 we started working on a specific laser plasma in cooperation with Dr. Jens Riedel from the Federal Institute for Materials Research (BAM) from Berlin. So far, this project resulted in two bachelor theses [233, 234] and one publication [235]. A further publication is currently in preparation.

In a unique experimental setup we focused the beam of the first harmonic of a Nd:YAG diode pumped solid state laser into the inlet chamber of our VUV spectrometer. During each laser pulse, a small plasma ball formed in the focus of the lens in front of the spectrometer's entrance slit. The chamber was additionally equipped with two copper electrodes, a discharge gas supply with an oppositely positioned active pumping stage and an orthogonally arranged optical fiber. This setup allowed us to cover a spectroscopic range between 40-1100 nm and simultaneously collect temporal charge profiles with clearly defined experimental conditions regarding plasma-gas pressure and composition. The spectroscopy yielded valuable information on prevailing species and their emission, and allowed us to clearly differentiate between the radiation of the plasma core and of the subsequently expanding plume. In a more theoretically oriented work, we estimated the plasma core dimension and the maximum amount of charge that was generated. These simulations were based on geometrical plasma boundaries from photographic close-ups, accurate temporally resolved laser light recordings, exact energy measurements and literature data on multiphoton ionization rates. The experimentally observed amount of

free electrons in one laser pulse corresponds well to the theoretical predictions. We found an interesting correlation between the applied voltage on the detection electrodes and the recorded current, in dependence of the plasma pressure. In the near future, newly acquired optical parametric oscillators will allow us to continue experiments regarding this remarkable plasma type with pulses from laser light ranging from 200 - 4500 nm.

2 Introduction and Theory

A laser induced plasma (LIP) in a gas is readily generated upon focusing a few millijoule of a nanosecond long Nd:YAG pulse. When sharply focused in a gas matrix to some $10^{13} \text{ W}\cdot\text{cm}^{-2}$, a visible plasma plume with a diameter of a few millimeter is created. The practical implementation is rather simple, but the theory is quite fascinating. Initially, the dense electromagnetic field accelerates some present free electrons up to several electron volts, which excite the atoms, promoting them into higher energy states. Due to the increased state density of these excited states, they are readily photoionized by subsequent photon absorption. This synergistic interplay between electron-induced excitation and subsequent photoionization of excited states initiates a highly efficient avalanche process. The exponentially increasing population of secondary electrons, further accelerated and energized by the incident laser radiation, leads to the formation of a region with rapidly increasing opacity to the light. This efficient process drives the gas to partial ionization approaching unity and facilitates an extraordinary accumulation of energy from the radiation field within a remarkably small primary focal volume. Ultimately, this situation culminates in a gas breakdown. Once the laser pulse extinguishes, this small focus volume has absorbed several tenths of the totally available radiation energy. In other words, a large energy gradient build up within nanoseconds, which subsequently depletes through rapid expansion, recombination, light emission and heat production. Processes that are accompanied by the characteristic cracking noise and the fascinating, exponentially decaying illumination of a visible volume we commonly define as the plasma region. Within microseconds the system is completely thermalized and ready for the next pulse when used with frequencies well below one kHz. In 1964 Meyerand and Haught were among the first publishing experimental results on a gas breakdown at optical frequencies with a sharply focused ruby laser beam [236]. Theoretical open questions were immediately addressed such as the origin of the initial free electrons or the description of quantum mechanical states that initially store the energy from the radiating field. About a decade later, in 1975, Morgan summarized the most important discussion threads and the results on which scientist commonly agreed on [237]. It was concluded that the initial electrons in fact stem from multiphoton ionization processes. Based on a simple energy balance with a photon wavelength of

1064 nm (1.17 eV), this process requires around 14 photons for an argon atom ($IE = 15.76$ eV). From a probability perspective this event seems to be very unlikely, since at least nine virtual states need to be created before the first resonant electronic energy level at 11.55 eV is reached. However, several arguments, calculations and experimental evidences lead to this incredible conclusion. Most importantly, the massive field density essentially lowers the potential energy barrier for the first electron to be removed, roughly comparable to the field ionization effect. The question on how free electrons can then rapidly absorb photons from the radiating field is explained by the inverse Bremsstrahlung, or free-free transitions. Here the free electron is quantum mechanically treated within the potential field of atoms and ions, which creates a certain state density that can be easily accessed with single photon energies. This mechanism allows for efficient energy deposition from a radiating field in a tiny volume of matter on a very short timescale, on which atomic motion and even electron diffusion are negligible. In the following phase of energy randomization into the motion of gas particles, in other words generating heat, temperatures of 10^5 K are realized, which is sufficient for intense electronic excitation. In addition, this tremendous gradient with the surrounding gas at room temperature results in an adiabatic expansion, shock wave formation and eventually to this characteristic cracking noise. The unique way of LIPs to form spatially and temporally well defined, extremely high energy density states of matter have paved the way for vast new implications in the last six decades. A range spanning from the ongoing attempt to ignite nuclear fusion, to the routine analytical application in laser induced breakdown spectroscopy (LIBS), where the rich and characteristic fluorescence of the extinction phase is used for elemental quantification.

In this contribution we characterize LIPs generated with the fundamental of a pulsed diode pumped Nd:YAG (30 mJ, 100 Hz, 6 ns) laser. Argon was used as the primary plasma gas at pressures between 400 and 1600 mbar, also with well-defined admixtures of N_2 , O_2 , CO_2 , H_2 and Ne. The available diagnostic tools allowed us investigating the plasmas in terms of the spectral resolved light emission between 40 and 1100 nm, the evolution of the radiation with sub-nanosecond temporal resolution and the evolution of charge formation. An in-depth discussion of our experimental results based on well-known concepts from literature will be given.

3 Methods

3.1 Laser and Plasma Chamber

A diode pumped Nd:YAG laser (Titan AC 30 MM, IB Laser, Berlin, Germany) provided $30 (\pm 5)$ mJ per pulse of the fundamental 1064 nm emission with a repetition rate of 100 Hz and a pulse width (fwhm) of 6 ns. The beam width at the exit is 0.15 cm with a

[illegible]

Moving the glass tube allowed to precisely center the plasma in front of the entrance slit of the VUV spectrometer. For electron emission measurements two plane, parallel copper electrodes with a distance of 18 mm enclosed the plasma volume (cf. section 3.5). A gas in- and outlet through the upper and bottom electrode, respectively, provided a continuous plasma gas flow of up to 300 sccm. An arrangement of two flow controllers (1000 sccm and 1 sccm) allowed the preparation of gas mixtures with ratios of up to 1 % regarding one minor component. To reduce contamination of the VUV spectrometer a small counter gas flow (~ 20 sccm) of the main plasma gas component was supplied through the entrance slit of the spectrometer into the plasma chamber. The pressure inside the chamber and the VUV spectrometer was kept constant between 400 and 1600 mbar with a manual downstream needle valve and a rotary vane pump, which was connected to the bottom electrode (cf. Figure 66(b)). The gas supply assembly in combination with the pressure downstream regulation allowed for switching times within a couple of minutes between two different, but constant mixing ratio settings. Prior to the operating conditions, the chamber as well as the VUV spectrometer were evacuated down to $2 \cdot 10^{-6}$ mbar. A gate valve between the spectrometer and the turbomolecular pump allowed for rapid separation from the pumps and run fill-up procedures with the main gas to the desired pressure. The leakage of the entire setup (plasma chamber and

spectrometer) was determined to $1.6 \cdot 10^{-5}$ mbar·L·s⁻¹. A tentative estimate with fill-up procedures in the order of 500 s and a 5 L chamber volume leads to a maximum impurity background level with laboratory air of roughly $1 \cdot 10^{-3}$ mbar or 1 ppmV with regard to a final pressure of 1 000 mbar. Throughout all experiments argon was used as the main gas, additionally purified to lower ppbV impurity levels. Minor gas components were neon, nitrogen, oxygen, carbon dioxide and hydrogen, all used without further purification from gas cylinders with stated purities between 99.999 % to 99.995 %.

3.2 VUV Spectroscopy (40-300 nm)

Emission spectra ranging from 40-300 nm were recorded with a modified ARC VM-502 VUV spectrometer (cf. section 3.1.4.1 in chapter II SPARK PLASMA). As described earlier the plasma center was positioned in front of the entrance slit with approximately 5 mm distance. Entrance slit widths of typical 0.5 mm to 1.0 mm were used. An MgF₂ coated parabolic and movable grating ($1\,200\text{ l}\cdot\text{mm}^{-1}$) reflected the radiation onto a 0.5 mm wide exit slit. A scintillator (sodium salicylate) coated lens was used to convert the dispersed VUV radiation into visible light peaking at around 420 nm. The fluorescent light was focused onto a photomultiplier tube (R928, Hamamatsu Photonics K.K., Shimokanzo, Japan) with a matching spectral response. The electrical signal was digitized, and transferred to a personal computer at a rate of 4 Hz. A custom Visual Basic (Visual Basic 2010 Express, Microsoft Corporation, Redmond, WA) program [59] was used for the synchronization of the spectrum scanning and data acquisition systems. The scanning speed of the grating was set to $20\text{ nm}\cdot\text{min}^{-1}$ resulting in approximately 13 data points per nanometer. With 100 Hz repetition rate of the laser one data point roughly represents the average of 23 single plasma pulses. The recorded spectra were not corrected with a wavelength dependent instrument response factor.

3.3 UV to NIR Spectroscopy (200-1 100 nm)

A fiber optic spectrometer AvaSpec-3648 (Avantes BV, Eerbeek, The Netherlands), connected to a widely transparent optical fiber (ZFQ-9866, 0.2 mm diameter, Ocean Optics, Dunedin, FL, USA) covered the spectral emission range from 200 to 1 100 nm. As depicted in Figure 66(b) the fiber was oriented perpendicularly to the incident laser light with central alignment to the plasma core. The fiber head was seamlessly surface-mounted to the quartz window outside of the VUV spectrometer flange, such that a distance of roughly 1 cm resulted between the plasma core and the fiber entrance. The configuration of the spectrometer allowed a fwhm-resolution of $\Delta\lambda = 0.7\text{ nm}$. Typical integration times were between 220 and 440 ms. Prior to the measurements, a wavelength calibration with a standard mercury lamp covered the range of 250 up to

550 nm. Notable deviation from literature values were observed at longer wavelengths. A wavelength dependent response factor was not determined for UV-VIS-NIR data correction.

3.4 Temporally Resolved Light Emission

Two silicon based photodiodes (DET025AFC/M, Thorlabs Inc., Dachau, Germany) with 122 ps response time and a spectral coverage from 400 to 1100 nm were connected to a 500 MHz and 5 GSamples $\cdot$ s $^{-1}$ oscilloscope (RTGE1054, Rohde & Schwarz GmbH&Co. KG, Munich, Germany). After a few hours of operation we frequently noticed a significant deterioration in the temporal response of the photodiodes due to the voltage drop of the batteries, which were then replaced by adequate power supplies.

3.5 Electron Emission Measurements

Charge formation is one of the most characteristic and valuable parameter to be determined in plasmas. In the present experimental setup we used two plane and in parallel aligned copper electrodes, placed at a distance of 18 mm (cf. Figure 66(b)). The plasma plume was vertically and horizontally centered between the electrodes, such that it was well covered by their surfaces. Voltages between 0 and -400 V and in the extended range up to -800 V were applied to the bottom electrode to repel electrons from the plasma zone to the opposite collector electrode. The latter was connected to the same oscilloscope as used for the temporally resolved light emission measurements with a 1 Ω or 100 Ω parallel resistor to ground. For secondary breakdown experiments in the extended range, a multimeter in parallel to a 100 Ω resistance to ground was used. Given the precisely known resistant values, the measured voltages were converted into currents and the currents were integrated over time to determine the total charges.

Though as short as possible electrical connections were used to minimize time delays as well as electromagnetic noise, we still observed significant sinusoidal interferences from the intense driving currents of the laser diode. Larger distances of connectors to the laser cables and a 1 MHz broad band filter helped to reduce noise signals.

4 Results

4.1 Geometry of the Visible Plasma Ball

Figure 67(a) shows a magnification of a typical plasma “ball” in argon at 1000 mbar, 30 mJ laser energy per pulse, 100 Hz repetition rate, and 6 ns pulse width (fwhm). For a clearer

view of the contrasting elements, the image is shown in black and white, and the edge of the ball is slightly retraced by a dashed line. At a 0.07 s exposure time of the camera, this picture sums seven single breakdowns. With a diameter of 0.34 cm the visible plasma volume measures $V_{visible} = 2.1 \cdot 10^{-2} \text{ cm}^3$ and appears nearly ideally spherical, except a small convexity to the right. The origin of this conus is not clear. It may be due to small spherical aberration that distorts the perfect Gaussian focus and thus causes a diffraction pattern with slightly changing electrical field distributions and high-intensity spots along the optical beam axis. In these *hot spots* more initial free electrons are generated and more energy can be deposited than in low field regions. Similar, but more pronounced observations with several distinct plasma balls, well separated by up to a millimeter along the optical axis were reported by Evans [237, 238], who developed the spherical aberration theory, and Korobkin et al. [239]. The projection of the conus back through the plasma center onto the plane of the lens, maps a circle with a diameter of $d_{beam} = 0.31 \text{ cm}$, which is in good agreement with the measured diameter of the unfocused beam directly before the lens. The center of the visible plume is located at a distance of $d_{focus} = 0.57 \text{ cm}$ from the lens surface, which is close to the working distance of $wd = 0.59 \text{ cm}$ specified relative to the plane surface of the lens at the design wavelength of 780 nm.

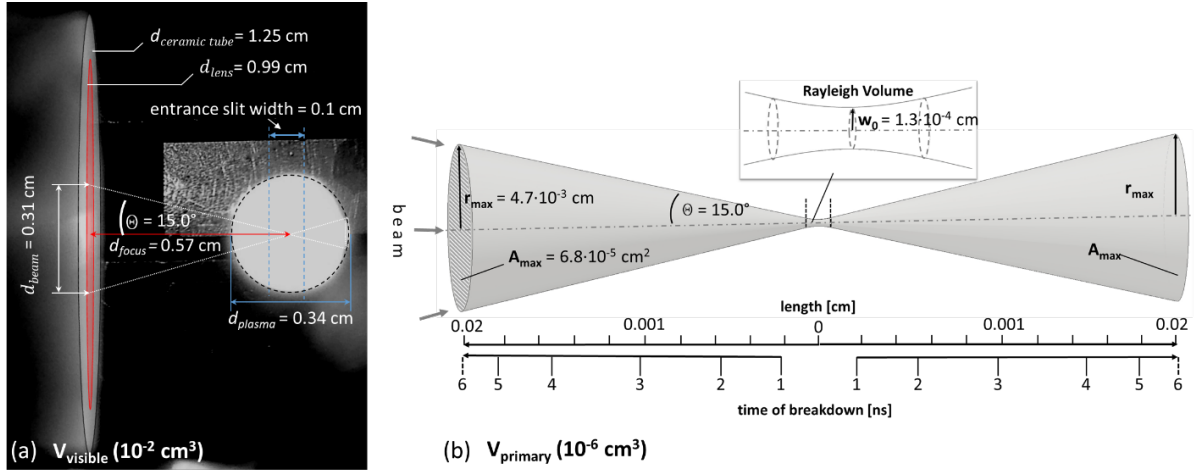


Figure 67: (a) Photograph of the visible plasma plume [233] and (b) draft of the approximated primary plasma volume (plasma core) initially heated through absorption of laser radiation via inverse Bremsstrahlung.

4.2 Formation of the Primary Plasma Core

Unfortunately, we cannot resolve the time evolution of a single breakdown with our simple camera and picture the much smaller plasma core or primary volume $V_{primary}$. That is the volume in which initial free electrons absorb a large amount of radiation energy through inverse Bremsstrahlung and heat it up in a couple of nanoseconds. To put it in another way: $V_{primary}$ represents the volume with the highest energy density during

a breakdown event. There are two possible ways to look at the initiation of this volume and to derive its size along the beam path:

(i) From the perspective of a pure inverse Bremsstrahlung mechanism without any contribution of atom-photon interaction we consider a scenario where a stray population of a few free electrons exists within the light path. Now we are interested in determining the minimum photon flux required to impart sufficient acceleration to these electrons to initiate an exponential growth in the electron-ion density through a purely electron-driven ionization cascade. Using the derived time-dependent photocurrent from a temporally-resolved laser energy experiment, we can identify the specific cross-sectional area along the light path and along the laser pulse progression where the photon flux density is sufficient to trigger the aforementioned electron-driven ionization cascade.

(ii) From the perspective of purely multiphoton ionization (MPI) events and their corresponding electron-ion yields along the beam path and along the laser pulse progression, we aim to determine the propagation distance from the focal point. This distance signifies the point within the laser beam where the cross-section is sufficient for the photon flux density to induce a single MPI event within this specific cross-sectional area. The reasoning behind this approach is that any differential volume segment along the beam path containing at least *one* MPI-generated electron will contribute to the heating process in $V_{primary}$ through the immediate pick up of radiation via inverse Bremsstrahlung.

In reality both mechanisms contribute to the final electron-ion population, as we will discuss later on.

4.2.1 Electron-Ionization through Inverse Bremsstrahlung

Though challenging to experimentally determine, it is possible to roughly estimate $V_{primary}$ with some calculations (cf. Figure 67(b)), neglecting any contribution of spherical aberration and electron diffusion out of the beam path during the laser pulse. Several studies support the assumption that electron diffusion is minimal during such short pulses[240]. Furthermore, it is reasonable to assume the positions of the atoms as stationary during the laser pulse. Gas kinetic theory predicts a mean displacement of merely 10 μm within the pulse width. The key idea to derive $V_{primary}$ in this approach is to identify the fraction of the focused beam path where the photon density is high enough to cause breakdown according to the electron-ionization mechanism induced by inverse Bremsstrahlung. To proceed, we must first determine the minimum photon flux Φ_{min} required to initiate such a breakdown. According to Wright [240] Φ_{min} [photons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$] as a function of the argon density n_{Ar} [cm^{-3}] is given by:

$$\Phi_{min} = 3.2 \cdot 10^{27} + 0.95 \cdot 10^{49} \cdot n_{Ar}^{-1} \quad (16)$$

This equation is derived from a kinetic approach considering the mean energy picked up by electrons in the radiation field, the energy losses via elastic collisions, the required mean energy to cause EI and a minimum amount of ionization events to initiate electrical breakdown. Typical experimental conditions of $n_{Ar} = 2.5 \cdot 10^{19} \text{ cm}^{-3}$ at 1000 mbar and 298 K lead to a breakdown threshold of $\Phi_{min} = 3.8 \cdot 10^{29} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. This result is in good accord with an extrapolation of experimental data by Ireland [241]. His work investigated the breakdown of argon using a Nd:YAG laser with pulse durations of 50 ns and 3 ns at various pressures. Furthermore, this value is also in good agreement with findings from Bebb and Gold for the initiation flux liberating one electron from argon by multiphoton ionization [242]. To proceed with the calculation of $V_{primary}$, the maximum laser emission rate R_{max} is needed. From the time resolved laser signal in Figure 69 and the known emission energy of 30 mJ per pulse, corresponding to $1.6 \cdot 10^{17}$ photons per pulse, one can derive the scale for the emission rate on the left axis of Figure 69. As shown, the maximum emission rate after 6 ns is $R_{max} = 2.6 \cdot 10^{25} \text{ photons} \cdot \text{s}^{-1}$. Dividing R_{max} by Φ_{min} leads to the maximum beam area of $A_{max} = 6.8 \cdot 10^{-5} \text{ cm}^2$, in which initial electrons can be generated along the light path at the maximum emission rate of the laser pulse (cf. Figure 67(b)). The next step is to determine the distance between the two surfaces of A_{max} to either side of the focal point as illustrated in Figure 67 (b). First, using basic trigonometry and the dimensions $d_{beam} = 0.31 \text{ cm}$ and $d_{focus} = 0.57 \text{ cm}$, we can determine the half focus angle as $\Theta = 15.0^\circ$ (cf. Figure 67(b)). Considering A_{max} and the corresponding radius $r_{max} = 4.7 \cdot 10^{-3} \text{ cm}$ a tangent calculation reveals that the breakdown condition is met within $\pm 2.0 \cdot 10^{-2} \text{ cm}$ of the focal point during a laser pulse. The next step is to determine the focal radius w_0 , assuming an ideal TEM₀₀ Gaussian beam profile [243]:

$$w_0 = \frac{2 \cdot \lambda \cdot \left(\frac{d_{focus}}{d_{beam}} \right)}{\pi} \quad (17)$$

With the laser wavelength $\lambda = 1064 \text{ nm}$, d_{focus} and d_{beam} of 0.57 cm and 0.31 cm respectively, a value of $w_0 = 1.3 \cdot 10^{-4} \text{ cm}$ is deduced, as illustrated in the inset of Figure 67(b). Neglecting the curved beam shape close to the ideal Gaussian focus one can draw a straight line from w_0 to r_{max} to either side of the focus ($\pm 2.0 \cdot 10^{-2} \text{ cm}$), rotate around the optical axis and obtain a doubly blunted cone with a total length of 0.04 cm and a volume of $V_{primary} = 1.0 \cdot 10^{-6} \text{ cm}^3$ (cf. Figure 67(b)). At this point the result shows that the initial volume $V_{primary}$ absorbing the entire energy in first place, is roughly four orders of magnitude smaller compared to the expanded, visible volume $V_{visible}$. Finally, we can also estimate the number of argon atoms involved in the primary energy

absorption process to be roughly $2.3 \cdot 10^{13}$ atoms, based on $V_{primary}$ at 298 K. The error in $V_{primary}$ caused by neglecting the real focal radius is below 10 %.

Using the fitted function for the time-dependent laser photon flux (cf. Figure 69) and the function for the cross-sectional area along the primary volume, we can calculate a corresponding timescale. As illustrated in Figure 67(b) this timescale signifies the points along the beam axis, starting from the focal point, when the photon flux density meets the breakdown criteria during the laser pulse.

4.2.2 Multiphoton Ionization

The ionization of argon with 1064 nm radiation ($IE = 15.76$ eV) requires 14 photons with a corresponding energy of 1.165 eV each. According to Morgan [237] the non-resonant multiphoton ionization rate constant k_{MPI} [s^{-1}] can be calculated as follows:

$$k_{MPI} = \sigma^a \cdot \Phi^a \cdot \frac{1}{\nu^{a-1} \cdot (a-1)!} \quad (18)$$

with the photon absorption cross section σ [cm^2], the photon flux density Φ [$photons \cdot cm^{-2} \cdot s^{-1}$], the radiation frequency ν [s^{-1}] and a the number of photons required for ionization. Typical values for σ are of the order of 10^{-16} [cm^2] [237], assuming the same cross section for each absorption step. The frequency of 1064 nm radiation is $\nu = 2.82 \cdot 10^{14} s^{-1}$ and essentially describes the inverse of the lifetime of each virtual state in that equation. The photon flux density significantly depends on the point in time of the laser pulse and the cross sectional area along the focused beam. Figure 68(a) illustrates the temporal and spatial dependence of the photon flux density for our experimental conditions, derived from the temporal progression of the laser light as explained in 4.2.1. The figure depicts how the photon flux density evolves along the light path, starting at the focal point (0 cm) and extending further, for various time points after the laser pulse initiation. Note the logarithmic scale of the z-axis, and that the mirrored propagation of Φ along the optical axis beyond the focal plane is not shown. Assuming a flux density of $10^{32} photons \cdot cm^{-2} \cdot s^{-1}$ we find the largest value for Φ in the focal region at the peak of the laser pulse (cf. Figure 69) at 6 ns. Along the optical axis the photon flux density rapidly falls off in either direction for the same point of time to approximately $10^{29} photons \cdot cm^{-2} \cdot s^{-1}$ after 0.02 cm. This value corresponds well to the spatial scale derived for $V_{primary}$ in Figure 67(b).

Using these data a specific rate constant k_{MPI} for each discrete position along the optical axis and for each time step during the laser pulse progression can be calculated. In addition, we simulated the ionization process with a numerical approach implemented in

a Python script. The script utilizes differential time steps dt of 15 ps and spatial steps dl of $0.2 \mu\text{m}$ along the beam path.

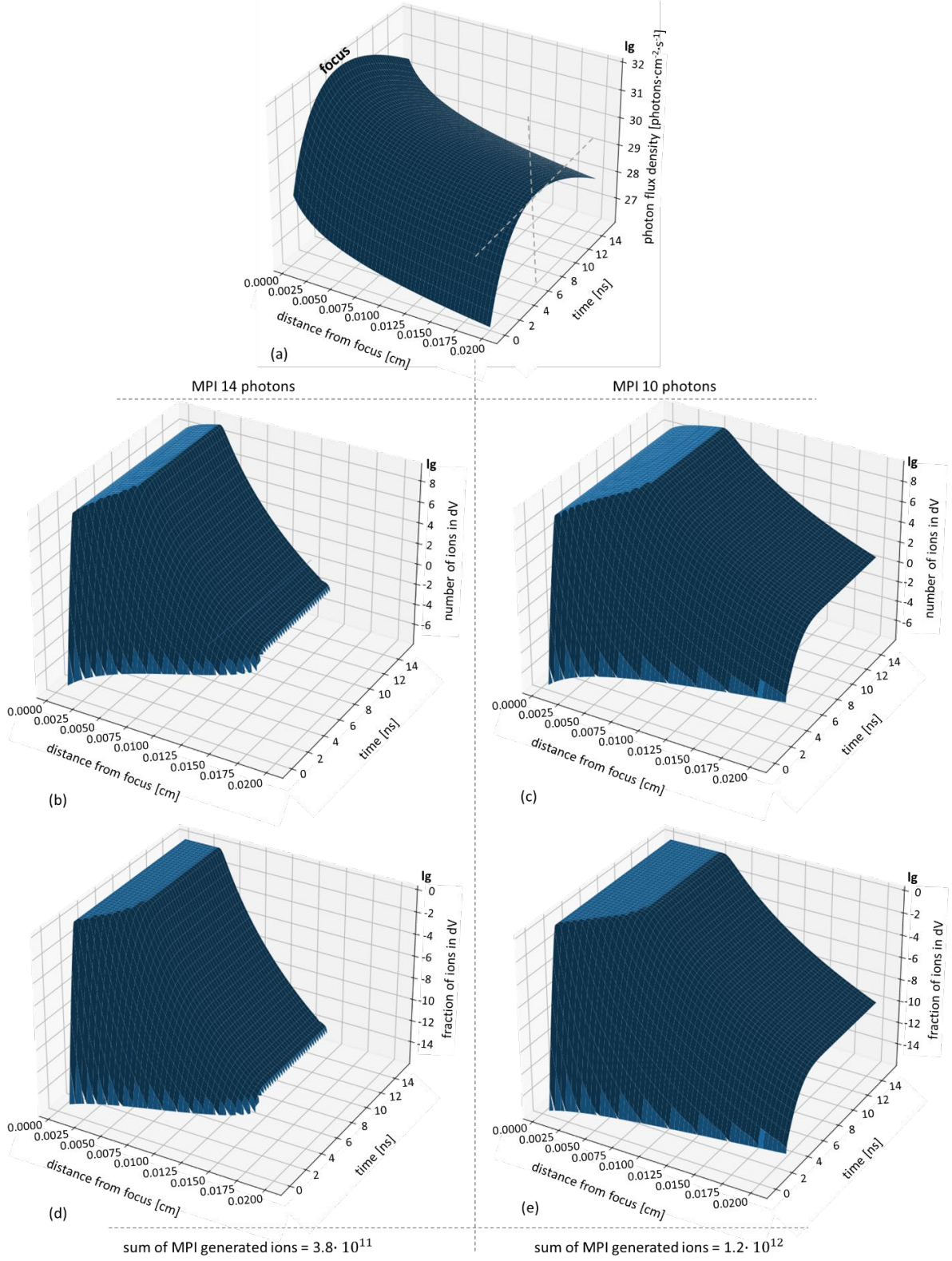


Figure 68: (a) Temporal and spatial dependence of the photon flux density derived from the time resolved laser light signal and the geometry of the focal region. (b)/(d) and (c)/(e) show the temporal evolution of the number and fraction of ions generated during a laser pulse for an argon MPI process with 14 photons and 10 photons, respectively.

The simulation assumes a gas density corresponding to 298 K and 1000 mbar, and requiring $a = 14$ photons to ionize argon. The results, presented in Figure 68(b) and (d), depict the number and fraction of ions, respectively, generated within a small volume element dV at each grid point. This volume element is defined by the beam cross-section at that distance from the focus and the differential length dl used throughout the simulation. Furthermore, we assumed a constant cross-section within each dl segment. However, as the distance from the focal plane increases, the beam cross-section expands. Consequently, the volume element dV of gas exposed to the laser radiation also increases, which translates to a larger number of neutral atoms available for potential ionization. This explains why the initial number of generated ions in dV appears lower near the focal plane (cf. Figure 68(b)), though we essentially calculate ionization yields of 100 % all the way up to 0.005 cm distance (cf. Figure 68(d)).

As we move away from the focus, the decreasing photon flux density rapidly reduces both the number of generated ions and the fractional ionization yield. At approximately 0.01 cm the simulation calculates roughly one ionization event (0 on the logarithmic scale) in dV , which presents the boundary of $V_{primary}$ according to our aforementioned definition (cf. 4.2). Hence, considering only the MPI process with $a = 14$, our simulations predict an extent of the primary plasma region along the beam axis which is roughly half of what we arrived at using a pure electron ionization approach (see Figure 67(b) for comparison). The volume of this initial region is $1.6 \cdot 10^{-7} \text{ cm}^3$ with a total number of $3.8 \cdot 10^{12}$ neutral argon atoms potentially available for ionization. The simulation further predicts 10 % ionization yield and thus a total number of $3.8 \cdot 10^{11}$ MPI events. Clearly, a strong anisotropic distribution of these initial ions is found along the beam path. As previously noted, within the focal region and up to a distance of 0.005 cm, the simulation calculates complete ionization of all neutral atoms. However, 5 μm further away from the focus, the fraction of ionized atoms drops by approximately 14 orders of magnitude. In the regions of $V_{primary}$ with MPI yields below unity, it is reasonable to assume that electrons rapidly pick up energy from the laser radiation via inverse Bremsstrahlung, speed up and ionize the remaining neutrals through EI. A maximum ion yield of $3.8 \cdot 10^{12}$ ions is expected within the plasma ball in this scenario. In the region of virtually 100 % MPI the free electrons are immediately accelerated as well and cause extensive electronic excitation of adjacent ions. Therefore, strong emission characteristic of Ar(II) transitions is anticipated exclusively from this region, which is in very good accord with our experimental observations, as detailed in section 4.6.1.

Using an exponent of $a = 14$ in the k_{MPI} expression in equation (18) represents the lower limit for the MPI rate. Experimental observations, however, have revealed that resonance or near-resonance conditions can significantly lower the value of a [237]. These resonances occur when the combined energy of an integral number of photons matches

closely with an allowed intermediate energy level of the target atom. The intense electromagnetic field of the laser pulse can further influence this process by shifting and broadening these intermediate energy levels, rendering resonance processes more likely. In case of argon, the first two resonant levels are located at energies of 11.55 eV ($3s^2 3p^5 4s^2 / 2 [^3/2]^\circ / J:2$) and 11.62 eV ($3s^2 3p^5 4s^2 / 2 [^3/2]^\circ / J:1$) [177] corresponding to nearly 10 photons (11.65 eV) from the Nd:YAG laser's fundamental radiation. Indeed, in argon values for the exponent a of nearly 10 were found experimentally under conditions comparable to the present study [244]. We therefore also simulated the ionization process in the primary plasma volume for k_{MPI} with $a = 10$ representing the upper limit for the MPI rate. The results are depicted in Figure 68(c) and (e). The simulations reveal that the region with 100 % multiphoton ionization yield extends from the focus up to a distance of 0.0075 cm. The farthest location where at least one ion is still generated in the differential volume dV via MPI is approximately 0.02 cm away from the focal point. This distance matches well with the results obtained using the pure electron ionization approach (cf. 4.2.1). As previously mentioned, $V_{primary}$ at a 0.02 cm boundary from the focal plane contains $2.3 \cdot 10^{13}$ neutral argon atoms. The simulation predicts that MPI within this volume generates a total of $1.2 \cdot 10^{12}$ ions, corresponding to an average ionization yield of 5 %. Assuming subsequent electron ionization via inverse Bremsstrahlung covering the remaining 95 % of neutral atoms within the primary plasma volume, the total expected ion yield is $2.3 \cdot 10^{13}$ ions. Also for this scenario the simulations show a strong non-uniform distribution of MPI-generated ions. Again, we anticipate that in regions with low ionization fractions (i.e., far from the focus), subsequent electron ionization processes dominate. Conversely, in the focal region with near-complete MPI ionization, significant electronic excitation of argon ions induced by free electrons is expected. Also in this scenario with $a = 10$, this excitation scenario leads to strong emission lines characteristic of Ar(II) transitions, originating exclusively from this highly ionized region.

In summary: While our simulations include some simplifying assumptions, they provide a good picture of the initially ionized region created by the laser pulse. These assumptions neglect the simultaneous occurrence of electron and photon induced processes, and assume negligible ion formation during the plasma expansion phase. Additionally, we assume that all detected ions originate in the primary volume, which is fully ionized first by MPI followed by further EI through inverse Bremsstrahlung. Despite these approximations, simulations for the two extreme MPI scenarios with exponential expressions for k_{MPI} of $a = 14$ and 10, respectively, provide a consistent picture. The primary volume likely extends 10-20 μm in both directions from the focal plane, with a total volume ranging from $1.6 \cdot 10^{-7} \text{ cm}^3$ to $1.0 \cdot 10^{-6} \text{ cm}^3$. This translates to a predicted number of generated ions between $3.8 \cdot 10^{12}$ and $2.3 \cdot 10^{13}$. The experimentally derived ion population of $6 \cdot 10^{12}$ falls within this range, as will be detailed later in section 4.4. This

result is in good agreement with other published values, typically around 10^{13} ions as reported by Morgan [237] and Meyerand et al. [236]. Furthermore, our experiments confirm that the predicted Ar(II) emission lines indeed originate from a very small, confined region within the plasma, as will be discussed in section 4.6.1.

4.3 Temporally Resolved Light Measurements

Figure 69 shows the time resolved light emission rate of the laser pulse (left scale) and the normalized plasma emission in the range of the spectral response of the photodiode (right scale).

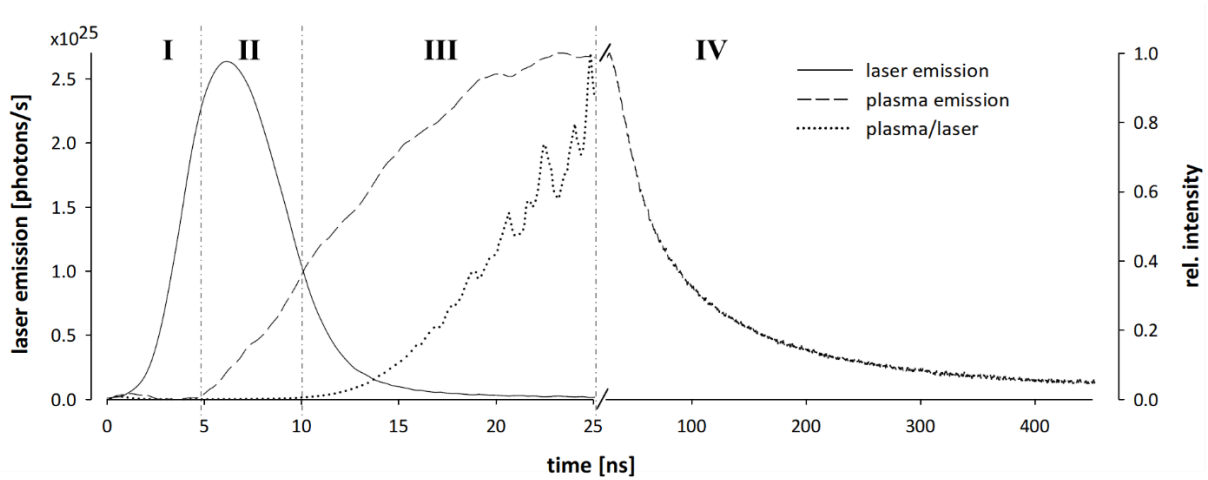


Figure 69 (data recorded by Dr. Rieger [233]): Time resolved laser and plasma emission with 100 % argon at 1000 mbar and a flow rate of 100 sccm. The photon flux was derived by normalizing the area of the photodiode's recorded signal to the respective total number of photons (with 30 mJ pulse energy) and subsequent numerical differentiation.

The same experimental conditions as described in section 4.1 apply (argon at 1000 mbar, 100 sccm volume flow). Note the different time scales for the rise and decay phase with a break at 25 ns. In addition, the ratio of the normalized plasma light emission and the laser emission rate is plotted between 0 and 25 ns (right scale). Four distinct regions of the plasma evolution are marked with roman numerals.

Region I: A laser induced plasma cannot rely on natural occurring free electrons produced by local radioactivity or cosmic rays. Their abundance is approximately 500 electrons per cm^3 [245]; in view of a total primary ionization volume of $V_{\text{primary}} = 10^{-6} \text{ cm}^3$ (cf. section 4.2) the probability of finding an electron in the focal region is negligible. Consequently, the first five nanoseconds are dominated by the generation of free electrons via multiphoton ionization, starting in the focal plane and extending up to 20 μm to either side with progressing photo current, peaking at 6 ns (cf. section 4.2.2).

Region II: We observe the first signs of plasma emission at around five nanoseconds. This indicates the start of fluorescence from argon atoms that were previously excited by

energetic electrons. These electrons have gained enough energy from the radiation field through the inverse Bremsstrahlung process. It is important to note that this excitation likely began earlier in region I, as fluorescence lifetimes can extend to several nanoseconds. We can tentatively identify the point of breakdown as the point where the system transitions from region I to region II. At about 6 ns, multiphoton ionization should be mostly completed. After this point, excitation and ionization will be primarily driven by the accelerated electrons (EI).

Region III: In this region, the processes of plasma emission and the primary volume expanding to form the visible plume become dominant, since the initial energy transfer from the radiation field to the electrons drops rapidly, also indicated by the exponentially increasing ratio between the laser and plasma emission. At 15 ns, this contribution to electron acceleration becomes negligible. Consequently, we expect no significant further acceleration of electrons. Finally, at 25 ns (the end of region III), the visible plasma plume should reach its maximum size, as shown in the photograph in Figure 67(a).

Region IV: At 25 ns the extinction phase follows with an exponential decay of the plasma emission over a period of more than 400 ns. In his bachelor thesis, Dr. Rieger calculated the first order decay rate constant as $1.0 \cdot 10^7 \text{ s}^{-1}$ which is a typical fluorescence constant [233]. The plasma radiation thus gradually fades away as a result of radiation, conduction of thermal energy, the removal of electrons and ions by diffusion and recombination. Finally local thermodynamic equilibrium with the surrounding gas is restored and ready for the next laser pulse (100 Hz) starting at $1 \cdot 10^7 \text{ ns}$. The same time scale is explicitly used to emphasize a key point: Each laser-induced plasma event is entirely independent of the previous one. By the time the next laser pulse arrives, the plasma has completely extinguished and the irradiated volume has returned for long to a state identical to the surrounding gas.

4.3.1 Dependencies of the Plasma Emission Characteristics

In his bachelor thesis, Dr. Rieger scrutinized the temporal evolution of plasma emission within the photodiode's spectral range between 400 and 1100 nm [233]. Particularly the delay time relative to the laser light, the rise and fall time and the maximum height of the recorded signal were of interest.

First of all, neither variations in the volume flow rate up to 350 sccm nor admixtures of CO₂, N₂, H₂, O₂ or Ne at mixing ratios up to 1 % had a measurable impact. Additionally, adjusting the repeller voltage (cf. Figure 66(b)) up to 350 V did not affect the recorded plasma emission either.

In contrast, pressure and laser intensity clearly affected the plasma emission. At a constant pressure of 1000 mbar of argon, the plasma emission intensity exhibited a linear increase with increasing laser pulse energy. This trend was observed within the range of

23 to 30 mJ per pulse. The limited laser output energy restricted the experimental range to a maximum of 30 mJ. Below 23 mJ, the plasma failed to ignite. Figure 70(a) depicts this linear trend.

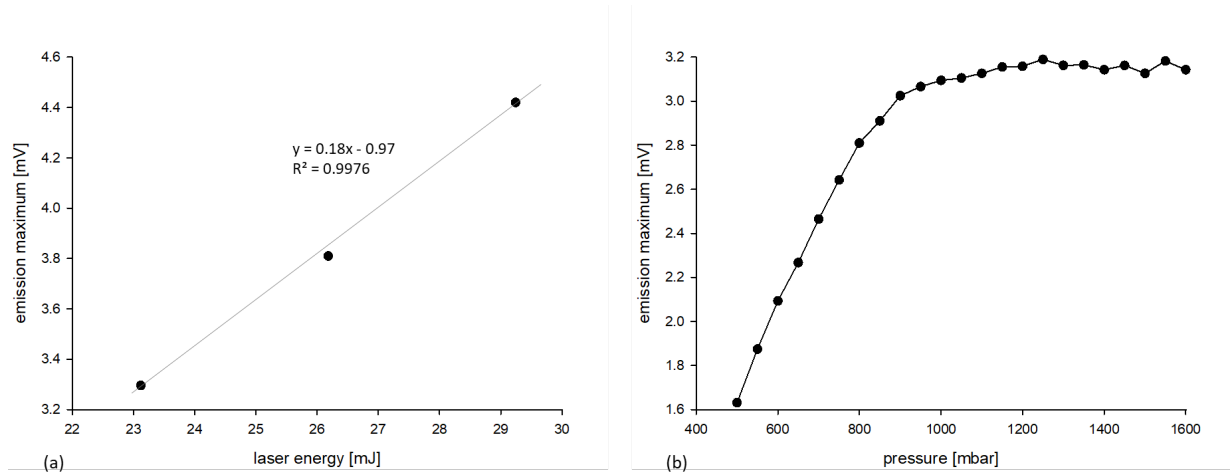


Figure 70 (data recorded by Dr. Rieger [233]): Plasma emission dependency (400-1100 nm) on (a) laser energy and (b) gas pressure.

The dependence of the maximum emission intensity on pressure exhibits a linear increase by a factor of two between 500 and 850 mbar, followed by saturation up to 1600 mbar, as shown in Figure 70(b). The delay time for the onset of plasma emission relative to the laser pulse exhibits a similar trend (data not shown). Between 500 and 850 mbar, the delay time decreases linearly by approximately 1 ns, from an initial value of 5.5 ns to 4.5 ns. This delay time then also plateaus at 850 mbar and remains constant up to 1600 mbar. The underlying mechanism for these observed trends with saturation starting at 850 mbar remains unclear and requires further investigation. Finally, Dr. Rieger also observed a steady increase of the fall and rise time of the emission slope by approximately 70 % in the investigated pressure range, however, without observing a distinct saturation point (data not shown). Below a pressure of 600 mbar, the plasma exhibited flickering behavior, and ignition became impossible below approximately 400 mbar.

4.4 Plasma Electron Measurements

In his bachelor thesis, Dr. Rieger also investigated temporally resolved plasma currents from which we derived absolute numbers of electrons present. According to Figure 71, the electron capture efficiency of the collector electrode (cf. Figure 66(b) for the configuration) reaches unity at a repelling voltage of approximately 220 V. This experiment confirms that the applied repeller voltage does not induce secondary ionization in this range, thus ensuring that only the initial plasma core electrons contribute to the collected signal.

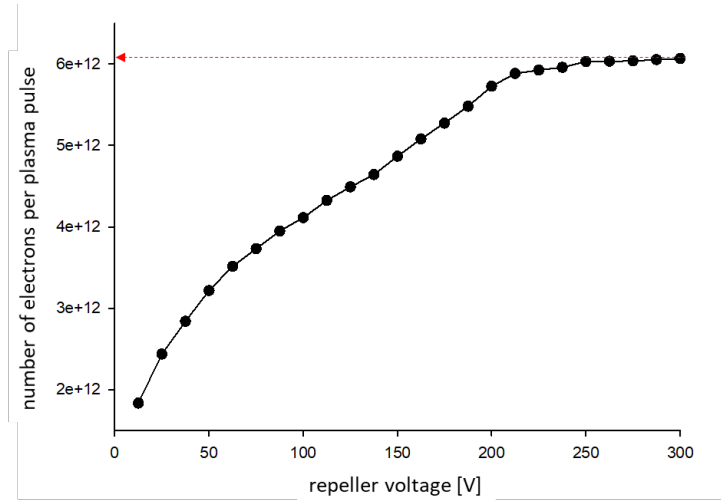


Figure 71 (data recorded by Dr. Rieger [233]): Absolute number of plasma electrons in dependence of the repeller voltage at 1000 mbar argon.

Each data point corresponds to an average of approximately 100 single plasma events. The voltage drop across a $1\ \Omega$ parallel resistor was detected temporally resolved with an oscilloscope. Using the time integrated signal we calculated the absolute number of electrons collected per plasma pulse to $6 \cdot 10^{12}$ electrons, assuming unit collection efficiency, which is in good agreement with the results of the simulations presented in section 4.2.2 (simulated number between $3.8 \cdot 10^{12}$ and $2.3 \cdot 10^{13}$ electrons). These results are also in good agreement with literature values of 10^{13} measured ion pairs under similar conditions, as reported by Morgan [237], Wright [240] and Meyerand and Haught [236]. It is noted, however, that these results completely neglect the occurrence of electron loss processes, e.g., through recombination. The extent of the latter was not further assessed in the present study.

Dr. Rieger further investigated electron currents in the extended voltage range of the repeller between -300 and -800 V for various pressure settings. As shown in Figure 72(a), for each pressure condition we observed the initial steady increase of the electron current followed by a plateau, signifying the aforementioned 100 % collection efficiency of core plasma electrons. Further increase of the repeller voltage lead to a distinct change in the slope of the curves for each pressure condition. This suggests the occurrence of a secondary breakdown phenomenon triggered by the additional electric field. The pressure dependence of this breakdown event is significant, affecting both the repeller voltage at which it occurs and the steepness of the corresponding electron current rise. At 1400 mbar, the breakdown point is observed at 650 V. This breakdown voltage decreases progressively to 540 V, 450 V, and 355 V for pressures of 1200 mbar, 1000 mbar, and 800 mbar, respectively. Plotting the breakdown voltage versus the corresponding pressure in this range reveals a perfect linear relationship, as shown in Figure 72(b). Furthermore, the steepness of the electron current jump associated with secondary breakdown diminishes with decreasing gas density. At lower pressures, the transition

from the plateau region to the secondary electron avalanche becomes smoother, although a small distortion in the slope remains even at the lowest pressure investigated. All pressure conditions finally reach similar electron current levels at the highest repeller voltage. While this secondary breakdown phenomenon is not within the scope of the present study on laser-induced plasma, it presents an intriguing avenue for further investigations. The exact underlying mechanism remains speculative and warrants further exploration.

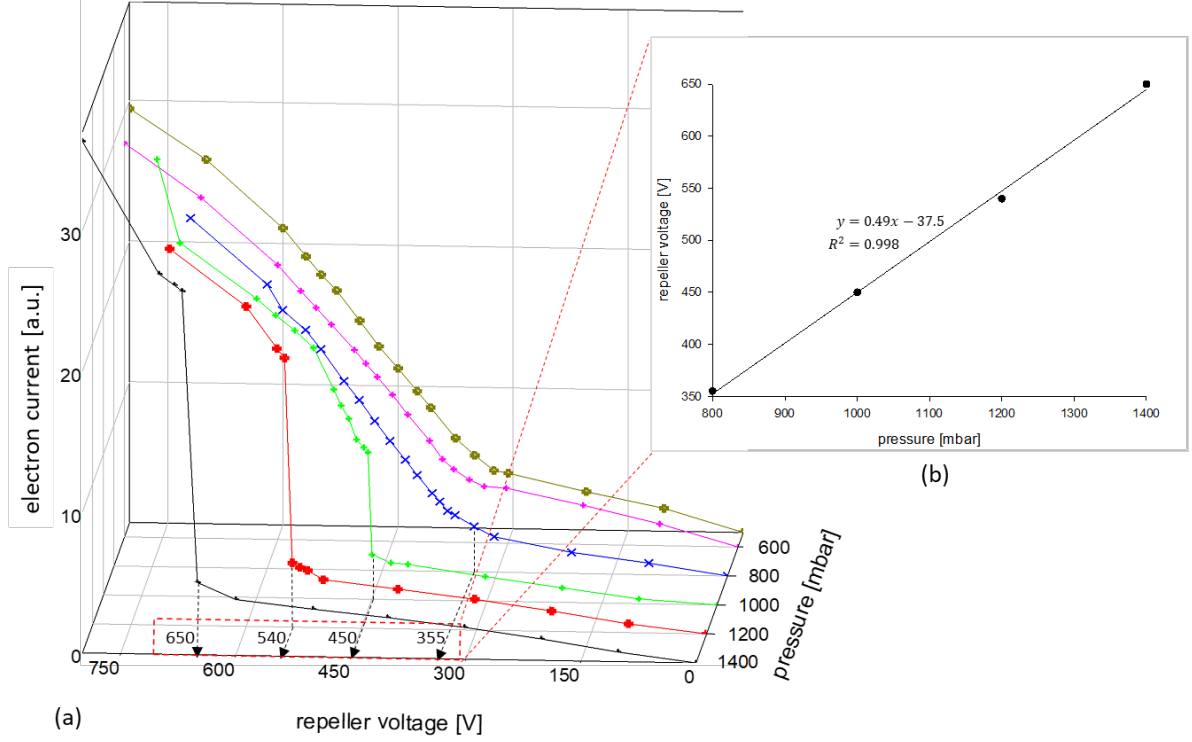


Figure 72 (data recorded by Dr. Rieger [233]): (a) Electron current on the collector electrode in dependence of the repelling voltage and argon gas pressure. (b) Secondary breakdown voltage as a function of argon gas pressure.

4.5 Energy Considerations

Similar to the experimental work from Meyerand and Haught [236], we considered the attenuation of the laser radiation - with and without plasma - as a measure for the totally absorbed photon energy through inverse Bremsstrahlung and to a lesser extent the MPI process. Following the light path in Figure 66(b), a certain fraction of the incoming Nd:YAG fundamental will be diffusively reflected from the opposed window after passing the plasma region and eventually be recorded by the UV-VIS-NIR spectrometer as stray light (cf. Figure 73). This approach requires negligible contribution of plasma scattered light and linear correlation between plasma absorbed laser radiation and stray light attenuation to yield reasonable data. Since no shift was observed between the recorded wavelength of the laser light with and without the plasma, the impact of plasma scattering

is assumed to be negligible, as reported by Ramsden and Davies [246]. To obtain the zero plasma signal of the diffuse 1064 nm radiation, we evacuated the chamber below the plasma breakdown pressure of around 400 mbar. Increasing the pressure back to 1000 mbar in the same setup with constant laser energy of 30 mJ per pulse provided, eventually caused the plasma breakdown and a reproducible attenuation of the laser stray light due to energy absorption by the plasma was observed. Comparison of the integrated signals resulted in 54.2 % attenuation. It is reasonable to assume that this amount of the laser radiation indeed remained within the plasma, which corresponds to an energy of 16.3 mJ per pulse. Considering the total number of $N_{Ar} = 2.3 \cdot 10^{13}$ atoms present in the primary volume (cf. section 4.2), this results in $\varepsilon = 7.1 \cdot 10^{-16}$ J per atom, which translates to a plasma core temperature of approximately $5 \cdot 10^7$ K in a thermally equilibrated system. Similar values were reported, e.g., by Browne [247]. A further estimation according to the Boltzmann equation

$$\frac{N_2}{N_1} = \exp\left(-\frac{IE_{Ar}}{\varepsilon}\right) \quad (19)$$

in a thermally equilibrated and simplified two state system with the number of argon atoms in the electronic ground N_1 and ionized N_2 state ($IE_{Ar} = 15.76$ eV = $2.5 \cdot 10^{-18}$ J) reveals 99.6 % ionization of the primary plasma volume with this amount of energy per atom.

These calculations are only rough estimates. They do not account for energy losses beyond ionization, for example. For the determination of a more precise quantitative thermal ionization degree, one would use the more elaborate Saha equation [248]. Nevertheless, these results are consistent and provide strong support for the description of the plasma core's dimension and dynamics outlined in section 4.2.

4.6 Spectroscopic Features

While laser-induced plasmas have been subject to intense research for several decades, following closely on the event of the introduction of powerful pulsed laser systems, surprisingly little data exist on the VUV emission for “simple” *gas*-phase plasmas, as those investigated in the present work. Particularly in the wavelength range below the typical transmission cut-off of LiF at 105 nm, such data are rarely available. As has been discussed for the spectroscopy of our spark plasmas (cf. section 3.1.4.1 in chapter II SPARK PLASMA), this additional range down to approximately 40 nm for high pressure plasmas requires enhanced experimental efforts, which may be one of the reasons for the rare data situation. In addition, less attention has been given to the spectroscopy of the primary plasma plume of such *gas*-phase LIPs since their usage in analytical or pure radiative

applications is rather limited [249]. In contrast, for laser-induced plasmas in *liquids* and *solids* a wealth of spectral data is available, covering the VUV and even the extreme ultraviolet (EUV) spectral region. These studies are motivated by applications of general interest and financial resources. For example, analyzing the carbon content in steel samples [250] or exploring new light sources generating specific types of radiation, e.g., the EUV-continuum observed with tin plasmas suitable for EUV-lithography scanners in the semiconducting industry [251], is driven by high financial interest as well as large scale industrial technology advancement. Even more spectral data are available for the UV-VIS-NIR range, since it is easier accessible. These studies have propelled the development of laser-induced breakdown spectroscopy (LIBS) for the elemental analysis in liquids and solids in the last three decades [252]. The emission spectra Dr. Bräkling recorded of the plasma plume (cf. Figure 67(a)) between 40-200 nm during his bachelor thesis in 2016 [234], are unique, despite the fact that laser induced plasmas have been around for more than six decades.

VUV

Figure 73 presents an emission spectrum of a typical laser induced argon plasma at 1000 mbar, with a flow rate of 25 sccm and a pulse energy of 30 mJ. The VUV part shows the range between 40 nm and 200 nm and the UV-VIS-NIR part the range from 200 nm to 1100 nm, respectively. A prominent peak is observed at around 60 nm, which corresponds to transitions between states of argon ions Ar(II) . This particular feature originates uniquely from the hottest, central region of the plasma, known as the plasma core (cf. section 4.2), and will be examined in more detail in section 4.6.1.

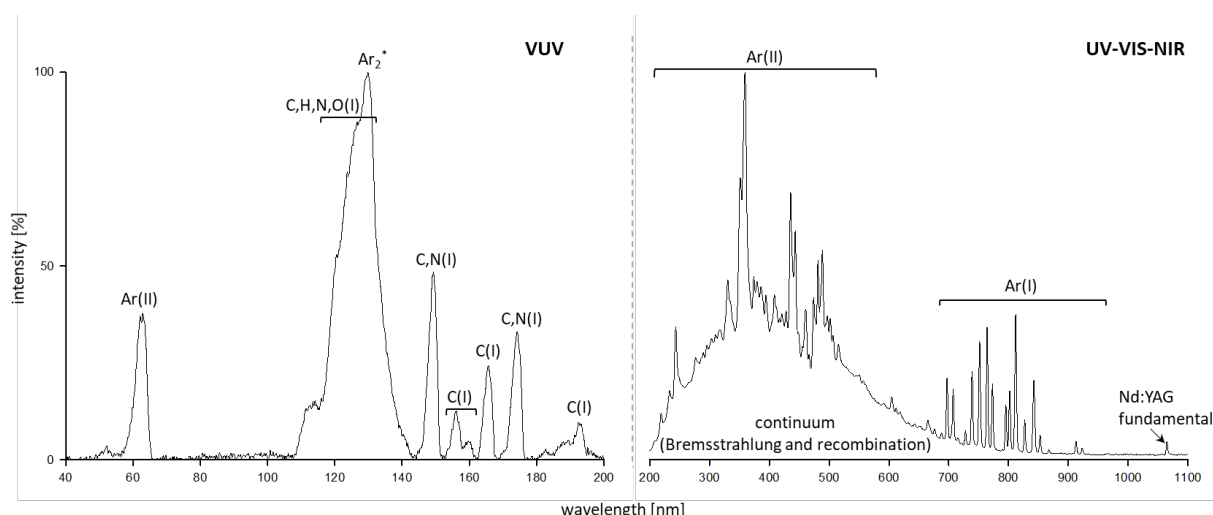


Figure 73 (data recorded by Dr. Bräkling [234]): Emission spectrum of a laser induced argon plasma at 1000 mbar, a flow rate of 25 sccm and 30 mJ pulse energy of 1064 nm radiation. The VUV part covers the range from 40 nm to 200 nm and the UV-VIS-NIR part the range from 200 nm to 1100 nm, respectively.

A further prominent peak assigned to argon is the second Ar_2^* continuum centered at 127 nm, with a line width of approximately 20 nm at half maximum. The formation of this

electronically excited molecule, its transition into the dissociative ground state and its rapid quenching by trace impurities is governed by mechanisms similar to those described for the Hopfield continuum of He_2^* in sections 3.2.2.1 and 3.2.2.3 in chapter II SPARK PLASMA. The two lowest electronic states of Ar_2^* , which we assume to be responsible for the observed emissions, are $^3\Sigma_u^+$ and $^1\Sigma_u^+$ with their potential wells at 10.6 and 10.7 eV above the dissociated electronic ground state atoms, respectively [253]. Their formation occurs in a termolecular reaction of $^3P_1$ or $^3P_2$ excited species and ground state argon atoms [91]. An elaborate spectroscopic overview of the associated specific band structures is given by Tanaka et al. [254]. The corresponding radiative lifetimes for the excited molecules are 6 ns and 2.86 μs , for the singlet [255] and triplet state [256], respectively. Due to the long lifetime of the latter, resonant energy transfer of the excimer to impurities is enhanced, as, e.g., reported for oxygen by Moselhy et al. [257] and from our own experimental work with the spark discharge [21]. We observe characteristic transitions of N(I) (119, 149 and 174 nm), O(I) (130 nm) and H(I) (121 nm) originating from laboratory air impurities. Some oil vapor contamination within the spectrometer housing gives rise to additional emissions of atomic carbon C(I) at 132, 146, 156, 160, 165, 173, and 193 nm. The limited resolution of the spectrometer did not allow the complete separation of some spectral features, particularly those overlapping with the Ar_2^* continuum. This hindered detailed, state-resolved mechanistic studies with this setup. Despite these limitations, the overall emission profile in the VUV - except for the Ar(II) emission - of this laser-induced plasma exhibits a remarkable similarity to other discharges operated at comparable argon pressures. This observation holds true regardless of the specific method used to initiate the discharge, as evidenced by our own spark discharge experiments [21], micro-hollow cathode discharges [257], and studies employing heavy-ion or electron beam excitation [90, 91]. Furthermore, the impact of trace impurities on the spectroscopic features appears identical across these methods. This suggests that the spectroscopic features observed in this wavelength range are essentially dominated by collisions, fostering the formation of the thermodynamically favored species. The higher the collision frequency and the higher the radiative lifetime of the involved excited argon species, the greater is the influence of trace impurities on the emission spectrum. In essence, this regime of the LIPs reflects the chemical dynamics governing the expansion and cooling phase of the plasma.

UV-VIS-NIR

In the wavelength range of 200 nm to 1100 nm we observed three distinct regions: (i) A continuum between 200 nm and approximately 750 nm associated with radiation from electron-ion recombination processes and Bremsstrahlung. (ii) Superimposed on this continuum, characteristic emissions from electronically excited singly ionized argon Ar(II) between 200 nm and 550 nm were recorded, followed by (iii) the Ar(I) emission

region from 690 nm to 925 nm with a multitude of characteristic transitions between neutral argon states. At 1 064 nm the reflected light of the laser radiation is clearly visible. Utilizing this reflection we quantified the energy absorbed by the plasma, as described in section 4.5. However, we did not detect any emissions attributable to impurities under these experimental conditions.

Differences between VUV and UV-VIS-NIR

The absence of impurity emissions in the time averaged UV-VIS-NIR spectrum is in stark contrast to the time averaged VUV region, although recorded under the same experimental conditions. UV-VIS-NIR emissions are primarily governed by prompt fluorescence, a rapid process occurring immediately after electronic excitation on the nanosecond timescale. As a result, the emission lines are less susceptible to interactions with impurities. In contrast, the VUV region between 100 nm and 200 nm depicts a time domain rather governed by chemical reactions involving collisions with metastable argon atoms, competition with the formation of the excited argon dimers Ar_2^* and their radiative decay. These processes occur on a longer timescale and favor the excitation of the most thermodynamically stable species present, which often include trace contaminants. Consequently, trace impurities have a much larger impact on the VUV emission spectrum as compared to the UV-VIS-NIR region. This is confirmed by our experimental results (cf. 4.6.3). This behavior is also in good agreement with the results obtained in helium spark plasmas, as detailed in section 3.2.2.2 in chapter II SPARK PLASMA.

4.6.1 Spectroscopy of the Plasma Core

Though we could not visualize the primary plasma volume with a camera, we partially resolved between some characteristic spectroscopic features of V_{primary} and V_{visible} . Figure 74 shows two emission spectra in the VUV region from 40 to 250 nm recorded with “pure” argon at 1 000 mbar. The first spectrum was obtained when the *center* of the visible plasma plume (cf. Figure 67(a)) was precisely *aligned* with the 0.1 cm entrance slit width of the VUV spectrometer. For the second spectrum the entrance slit width was reduced to 0.05 cm and the focusing lens (cf. Figure 66(b) and Figure 67(a)) was slightly moved causing a minor *misalignment* with the entrance slit, as depicted in Figure 74. This experimental modification caused minor changes for the spectral features between 100 nm and 250 nm. As expected, the total intensity dropped by approximately 40 % and the resolution slightly increased, while the peak positions and relative intensities were not affected at all. The most pronounced change, however, was observed in the region *below* 100 nm. Caused by the small *misalignment* of the plasma ball with the spectrometer’s entrance slit, the large peak of ionic Ar(II) transitions from 55-65 nm with its maximum at 62 nm completely vanished. This observation is readily explained: In the

first case, the VUV spectrometer sampled light from the core plasma *and* the entire plasma plume, whereas in the case of *misalignment* the slits masked the *primary* plasma volume V_{primary} emission entirely and only light from the considerably larger V_{visible} plume was recorded. This experimental finding strongly suggests that electronically excited ions are *exclusively* formed in this primary volume, as sketched in Figure 67(b) and discussed in sections 4.2.1 and 4.2.2. The independence on both volume flow and admixtures in this specific Ar(II) spectroscopic feature also suggests that it does not originate from a collision-dominated region. This is in contrast to the VUV range between 100 and 200 nm, as discussed above and which will be explored in more detail in the following sections.

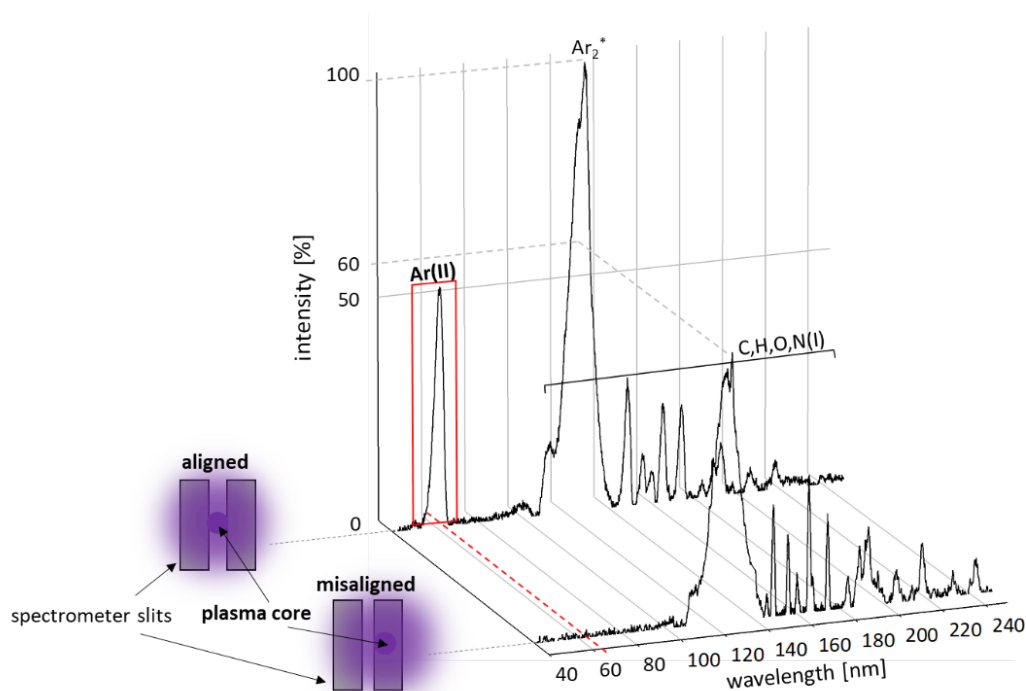


Figure 74 (data recorded by Dr. Bräkling [234]): Experimental indication that the Ar(II) emission originates exclusively from the core region of the laser-induced plasma. A slight misalignment of the plasma plume relative to the entrance slit of the VUV-spectrometer completely eliminates the Ar(II) feature, while all other spectral features remain present with only a minor decrease in intensity. This observation suggests that the Ar(II) emission zone has a distinct spatial distribution compared to the emitting regions of other species observed in the spectrum.

4.6.2 Emission Dependency on Volume Flow Rate

Figure 75 presents two VUV spectra recorded at flow rates of 25 sccm and 250 sccm, respectively. The pressure was maintained constant at 1000 mbar. Consistent with the previous discussion, the Ar(II) emission remains virtually unaffected by the flow rate change. In contrast, the emissions from impurities in the remaining spectral region show a significant decrease, accompanied by a rise in the Ar_2^* dimer continuum. This further reinforces the notion that the Ar(II) emission, as compared to other emitting species observed, originates from a distinct spatial region in the early stages of the plasma, likely a region with minimal collisional interactions such as the plasma core. The decrease in

impurity emission is likely due to the introduction of cleaner argon gas. As the flow rate increases, the cleaner gas displaces the more impure background gas from the focal region of the laser beam, resulting in the dominance of the pure argon species in the emission spectrum. It is important to note that the UV-VIS-NIR region (cf. Figure 73) remains entirely unaffected by the order-of-magnitude increase in argon flow rate.

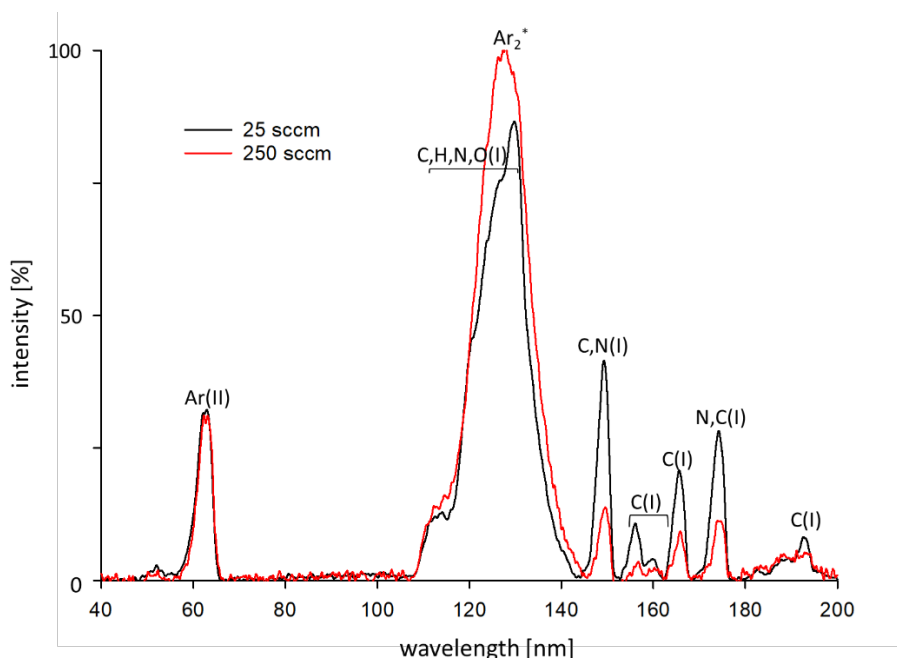


Figure 75 (data recorded by Dr. Bräkling [234]): Spectra recorded at argon volume flow rates of 25 sccm and 250 sccm, respectively. The pressure remained constant at 1 000 mbar.

4.6.3 Admixtures of Ar with O₂, H₂, N₂ and CO₂

In his bachelor thesis research work, Dr. Bräkling explored the effects of various minor components added to the laser-induced argon plasma [234]. He investigated admixtures of oxygen, hydrogen, nitrogen, and carbon dioxide, ranging in mixing ratios from 0.025 % to 1.0 %. Figure 76 presents the data for each series at a mixing ratio of 0.1 % alongside the corresponding pure argon spectrum measured at the beginning of each series for comparison.

The emission around 60 nm, assigned to Ar(II) transitions, remains largely unaffected by the addition of minor components of up to 0.1 %. For oxygen, nitrogen, and carbon dioxide, this holds true for even at their largest mixing ratio of 1 % (data not shown). This again fully supports the notion of the Ar(II) emission originating from a distinct spatial region in the early stages of the plasma evolution, likely a region with minimal collisional interactions such as the plasma core. Interestingly, hydrogen behaves differently. Even at a low mixing ratio of 0.1 %, a small decrease of the Ar(II) emission is observed. This effect becomes more pronounced at 1 % H₂, leading to a nearly 20 % reduction of Ar(II)

intensity. This suggests that hydrogen has a specific influence on the initial plasma formation and core region, unlike the other added gases, within this mixing ratio range. This behavior is also evident in the UV-VIS-NIR spectrum (data not shown).

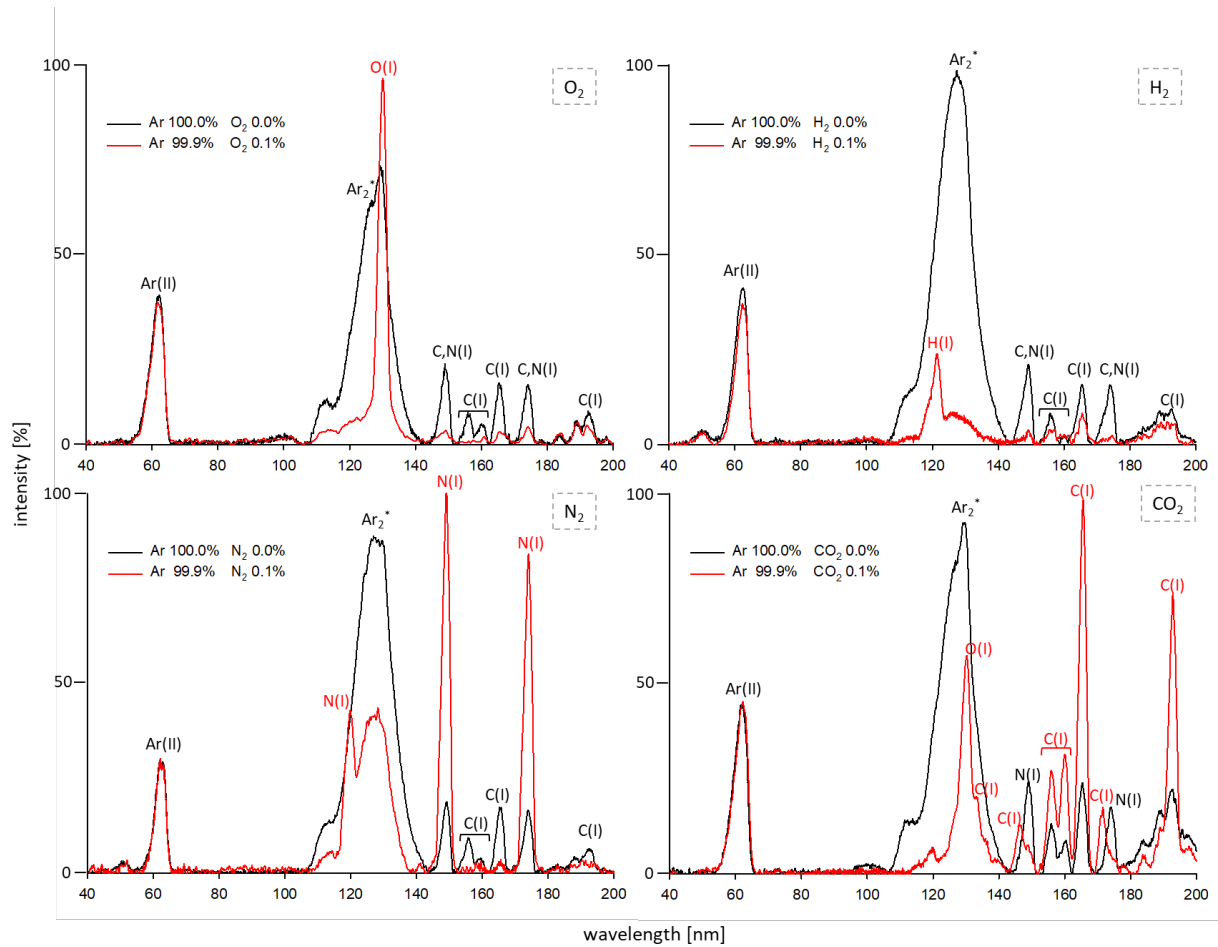


Figure 76 (data recorded by Dr. Bräkling [234]): Spectra of laser-induced argon plasmas with and without 0.1% addition of the minor components O_2 , H_2 , N_2 and CO_2 . Total volume flow rate was maintained at 100 sccm and the pressure remained constant at 1000 mbar.

While the addition of oxygen, nitrogen, and carbon dioxide, respectively, results in the appearance of some characteristic lines (e.g., O(I) at 777 nm), even at 1 % mixing ratio these lines remain below 10% of the maximum intensity. In contrast, hydrogen significantly reduces the continuum emission between 200 nm and 750 nm in the UV-VIS-NIR region, an effect not observed with the other gases. This observation strengthens the argument that under these conditions, hydrogen uniquely interacts with the plasma core and the expanding plasma plume. Unlike the other gases, hydrogen appears to interfere with the Bremsstrahlung radiation and recombination processes between electrons and argon ions.

The region between 100 nm and 200 nm in each spectrum of Figure 76 showcases a clear trend. The addition of dopant gases effectively quenches the Ar_2^* continuum emission through collisions, favoring the characteristic emission lines of the neutral atoms of the

added gas. Additionally, existing impurity emissions decrease significantly in favor of the dopant's emission. For 0.1 % O₂, the dominant feature becomes the characteristic O(I) line at 130 nm, with the Ar₂^{*} continuum virtually disappearing. For 0.1 % H₂ mixing ratio, the Lyman-alpha line of hydrogen appears at 121 nm, with some residual Ar₂^{*} emission. The overall emission intensity, however, is significantly reduced, which is not the case for the other gases. For 0.1 % N₂ addition, three characteristic N(I) lines at 119, 149, and 174 nm become prominent, while the Ar₂^{*} emission drops by nearly 60 %. For CO₂ with 0.1 % mixing ratio, emission lines for both carbon and oxygen are observed. The O(I) line remains at 130 nm, while C(I) emission appears at multiple wavelengths (132, 146, 156, 160, 165, 173, and 193 nm). The Ar₂^{*} emission is completely quenched.

Interestingly, the addition of neon at similar mixing ratios had no noticeable effect on either the VUV (100-200 nm) or UV-VIS-NIR spectra. This is attributed to the higher energy levels of excited neon states compared to excited argon species.

5 Conclusion and Outlook

In this chapter, laser-induced plasmas generated with the fundamental of a diode pumped Nd:YAG laser (30 mJ, 100 Hz, 6 ns) were characterized. Argon was used as the primary plasma gas at pressures between 400 and 1 600 mbar, also with well-defined admixtures of N₂, O₂, CO₂, H₂ and Ne. The available diagnostic tools allowed to investigate the plasmas in terms of wavelength-resolved light emission between 40 and 1 100 nm, the evolution of the total radiation with sub-nanosecond temporal resolution and the evolution of charge formation.

Imaging of the visible plume was used to characterize the overall plasma extent and with MPI simulations a detailed picture of the plasma core and its theoretical contribution to the total electron yield and its dynamics were obtained. Electron current measurements experimentally validated the expected charge amount within an order of magnitude. These experiments revealed a secondary breakdown phenomenon with perfectly linear relationship between pressure and the breakdown voltage. This result warrants further exploration.

Temporally resolved light emission analysis of the VIS-NIR spectral range allowed differentiating the plasma evolution into four distinct phases: (i) Multiphoton ionization (MPI), (ii) inverse Bremsstrahlung and breakdown, (iii) plasma expansion, and (iv) plasma extinction.

Despite the long history of laser-induced plasmas and their vast applications, data on the generated gas-phase plasma balls in the VUV (40 nm-200 nm) alongside the UV-VIS-NIR range under the same experimental condition are scarce. Therefore, the spectra

presented here are rather unique. The Ar_2^* continuum was readily identified in this region, and we observed its dependence on gas admixtures. Interestingly, the behavior of the VUV spectrum and its response to changes in pressure and gas composition show striking similarities to other discharges operated at similar argon pressures. This consistency holds true regardless of the specific discharge initiation method, which suggests that this spectral regime is dominated by collisional processes, leading to the formation of the most thermodynamically favored radiating species.

One intriguing exception emerged - the observation of an emission line at 60 nm uniquely attributed to Ar(II) . Unlike the remaining part of the VUV spectrum, this line exhibited remarkable resilience. It remained unaffected by changes in flow rate or most admixtures and only disappeared upon small misalignments with the spectrometer's entrance slit. While the overall spectral intensity slightly dropped upon misalignment, the Ar(II) line vanished. These observations point towards a spatially localized source with minimal collisional interactions, likely originating from the initial plasma core. Future investigations employing a micrometer stage for the focusing lens will map the spatial distribution of Ar(II) emission along the spectrometer entrance slit. This approach will essentially provide an experimental image of the plasma core based on the distribution of the Ar(II) emission. Additionally, time-resolved measurements hold promise for differentiating contributions from the primary and visible plasma volumes.

The UV-VIS-NIR region (200-1100 nm) was dominated by emission lines of Ar(I) and Ar(II) , along with a wide continuum attributed to electron-ion recombination and Bremsstrahlung radiation. Interestingly, increasing the mixing ratio of most admixtures up to 1 % had minimal impact on this spectral region. However, hydrogen acted as an exception, significantly reducing the continuum intensity. This observation warrants further investigation to understand the specific interaction between hydrogen and the plasma core, potentially involving its influence on Bremsstrahlung and recombination processes.

Finally, it is instructive to compare the spectroscopic observations of helium spark plasmas (discussed in section 3.2.2.2 in chapter II SPARK PLASMA) with the laser-induced argon plasmas presented here. Firstly, the quenching effect of the helium dimer continuum radiation by molecular impurities is at least two orders of magnitude stronger in helium plasmas. Secondly, the UV-VIS-NIR spectra of helium discharges reveal significantly more pronounced features from added gases compared to those observed in laser-induced argon plasmas. This is partially attributed to the inherently "cleaner" helium spectrum, with a substantially lower background due to the absence of continuum radiation.

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Notation and Terminology

$\text{\AA}$	Ångström
α	first Townsend coefficient
$\gamma_{i,p,m}$	second Townsend coefficient for electron release through ions, photons, metastables
ΔE_x	energy difference between two points along a repulsive ground state potential energy curve
ΔR	atom-atom separation
ε	energy
ε_0	vacuum permittivity
λ	mean free path; wavelength
λ_D	Debye length
μ_e	electronic dipole transition moment
ν	vibrational frequency
σ	absorption cross section
τ	lifetime
φ	quantum yield
Φ	photon flux density
$\Phi_{\min}$	minimum photon flux density
$\chi_{n,v''}$	nuclear wave function upper state
$\chi_{m,v'}$	nuclear wave function lower state
Ω	Ohm, electrical resistance
$[F]^+$	ion fragment
$[M]^+$	analyte cation
$[M+H]^+$	protonated analyte ion
$[M-H]^+$	de-hydrated analyte cation
a	number of photons required for ionization
A	ampere; Einstein coefficient for spontaneous emission; coefficient in Paschen's law
$A_{\max}$	maximum beam area in which initial electrons can be generated
B	coefficient in Paschen's law; magnetic field
API	atmospheric pressure ionization
APLI	atmospheric pressure laser ionization
APPI	atmospheric pressure photo ionization
ASMS	American Society for Mass Spectrometry
BNC	Bayonet Neill–Concelman connector
BTX	benzene, toluene, xylene mixture
c	compound concentration
cAPI	capillary atmospheric pressure ionization
CCD	charge coupled device
CESE	capillary electro-kinetically separation
cf.	refer to

CID	collisional induced dissociation
cm	centimeter
d	distance; transition dipole moment
d_{beam}	laser beam diameter
DC	direct current
d_{focus}	distance of the plasma plume center to the lens surface
DPSS	diode pumped solid state laser
E	electrical field
e	elementary charge
EMF	electromotive force
E_r	reduced electrical field strength
EUV	extreme ultraviolet
eV	electronvolt
FAME	fatty acid methyl ester
FFKM	perfluoroelastomer
$f_{p,m}$	geometrical factors for photons/metastables to reach the cathode
f_p	plasma frequency
fwhm	full width half maximum
GB	gas phase basicity
GC	gas chromatography
h	Planck constant
HV	high voltage
Hz	Hertz, frequency (per second)
i	current
i.e.	that means
i_0	initial current
ICP	inductively coupled plasma
IE	ionization energy
K	Kelvin
kB	Boltzmann constant
kHz	kilohertz
k_{MPI}	multiphoton ionization rate constant
KTP	potassium titanyl phosphate
kV	kilovolt
$k\Omega$	kiloohm
L	liter
l	lines
LIBS	laser induced breakdown spectroscopy
LOD	limit of detection
M	molar
m/z	mass-to-charge ratio
mA	milliampere
mg	milligram
mol	unit for the number of $6.022 \cdot 10^{23}$ countable entities
MPI	multi photon ionization
MS	mass spectrometer/spectrometry
$M\Omega$	megaohm
n	gas density
n_e	electron number density

Notation and Terminology

nF	nanofarad
N_i	sum of electrons from a single avalanche
N_{II}	mean number of liberated electrons from the cathode by the cations after each avalanche
NIR	near-infrared
nm	nanometer
$N_{p,m}$	number of photons and metastables per ion formed in one avalanche
OD	outer diameter
OES	optical emission spectroscopy
OPO	optical parametric oscillator
p	pressure
PA	proton affinity
PID	photo ionization detector
PMT	photo multiplier tube
ppbV	parts per billion per volume
ppmV	parts per million per volume
pptV	parts per trillion per volume
PVD	physical vapor deposition
R&D	research and development
REMPI	resonance enhanced multi photon ionization
$r_{\max}$	maximum radius of laser beam
$R_{\max}$	maximum laser emission rate
RF	radio frequency
RSD	residual standard deviation
rxn	reaction
S/N	signal to noise
sccm	standard cubic centimeter per minute
slm	standard liter per minute
SPI	single photon ionization
SSQ	short segmented quadrupole
T	temperature
t	time
Td	Townsend
T_e	electron temperature
TOF	time-of-flight
U	electric potential
U	DC voltage
UA	voltage at which the first avalanche process occurs
UB	breakdown voltage
UV	ultraviolet
V	volt
v	vibrational quantum number
V_{visible}	visible plasma volume
V_{primary}	primary plasma volume
VIS	visible
VUV	vacuum-ultraviolet
W	Watt
wd	lens' working distance
w_o	focal radius

