

Measurement of the electron density in Transient Spark discharge

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Abstract

This paper presents our measurements of the electron density in a streamer-to-spark transition discharge, which is named transient spark (TS), in atmospheric pressure air. Despite the dc applied voltage, TS has a pulsed character with short (~ 10 – 100 ns) high current (> 1 A) pulses, with a repetition frequency on the order of kHz. The electron density $n_e \sim 10^{17}$ cm $^{-3}$ at maximum is reached in TS with repetition frequencies below ~ 3 kHz, using relatively low power delivered to the plasma (0.2–3 W).

The temporal evolution of n_e was estimated from the resistance of the plasma discharge, which was obtained by a detailed analysis of the electric circuit representing the TS and the discharge diameter measurements using a fast intensified charge-coupled device (iCCD) camera. This estimate was compared with n_e calculated from the measured Stark broadening of several atomic lines: H $_{\alpha}$, N at 746 nm, and O triplet at 777 nm. Good agreement was obtained, although the method based on the plasma resistance is sensitive to an accurate determination of the discharge diameter. We have found that this method is also limited for strongly ionized plasmas. On the other hand, a lower n_e detection limit can be obtained by this method than from the Stark broadening of atomic lines.

Keywords: electron density, plasma resistance, Stark broadening, transient spark, self-pulsing discharge

(Some figures may appear in colour only in the online journal)

1. Introduction

Non-thermal plasma generated by electrical discharges can initiate chemical reactions in normally inert gaseous mixtures. The crucial parameter for the assessment of the plasma reactivity is the electron density n_e , since the whole non-thermal plasma chemistry is initially induced by the high energy electrons. Various experimental techniques have been used for the electron density measurement in plasmas. Commonly used laser spectroscopic methods are based on interferometry [1–3] and Thomson scattering [4]. Optical emission spectroscopy (OES) can also be used. A review of this topic was recently written by Ivkovic *et al* [5]. The most common OES method for the n_e measurement is based on the Stark broadening of atomic emission lines. The Stark broadening of tens of lines of various species have already

been studied (see [6, 7] and the references therein). The current can be state-of-the-art in Stark broadening theory as a theoretical basis for diagnostics of low temperature plasmas in gas discharges has recently been given by Stehlé *et al* [8].

Hydrogen-like and helium-like lines are the most sensitive to Stark broadening and they are the most commonly used for the determination of electron density in the plasma. The non-hydrogen lines of heavier neutral atoms are less sensitive to the Stark broadening, so they cannot be used for such low electron densities as hydrogen ones. At low n_e , the Stark broadening is also limited by other types of spectral lines broadening (instrumental, Doppler, Van der Waals). Except for the instrumental broadening, there are a variety of influences on the final line broadening in different types of plasma [9]. Recently, Palomares *et al* [10] showed that if the line fitting procedure is used to separate the effects of the different

broadening mechanisms, then the Stark broadening can be used, even below its theoretical validity regime. This was validated by Thomson scattering measurements, and the results show the agreement within 20% [10].

At high electron densities, the use of the H_β spectral line for the determination of the electron density is limited to n_e less than $6 \times 10^{17} \text{ cm}^{-3}$ due to the strong Stark broadening and spectral proximity of other Balmer series lines such as H_δ [11]. The H_α line enables measurements of the electron densities of up to 10^{19} cm^{-3} for otherwise identical plasma conditions because it is typically by a factor of 4 narrower than the H_β line [11]. However, there is a fairly quantitative agreement between measured and calculated widths, shifts, and profiles but only for n_e below approximately 10^{18} cm^{-3} , serious disagreements were found beyond $n_e \approx 10^{19} \text{ cm}^{-3}$ [12].

The use of lines of heavier atoms is the only alternative when hydrogen is not present, or at high electron temperatures where hydrogen is fully ionized [5]. The most intense atomic lines in the atmospheric pressure air plasmas are typically the lines of atomic oxygen and nitrogen. The broadening of the N atomic line at 746 nm was also recently used to diagnose a nanosecond repetitively pulsed (NRP) discharge [13]. The quadratic Stark effect of N given by Griem [14], with the correction introduced by Konjević [15] was used to do this. The whole procedure, including the handling of Van der Waals and instrumental broadening, was also described in [13] for an electron temperature of $T_e = 10\,000 \text{ K}$.

The difficulty with the Stark broadening is that it depends not only on n_e but also on electron temperature T_e and ion dynamics. This is not the case for the H_β line, where the dependence of Stark broadening on T_e is very weak. It is also relatively insensitive to ion dynamics, except for the line center dip [8]. This is the reason why H_β is frequently preferred over the H_α line for the n_e calculation, even if the intensity of the H_α line is much stronger, and it is usable for higher electron densities. The calculation of n_e from the full width at the half maximum (FWHM) of H_α line is difficult due to the sensitivity to electron temperature and ion dynamics. However, Gigosos *et al* [16] showed that it is possible to avoid these difficulties using the full width at the half area (FWHA) instead of FWHM. Their calculations cover the range of electron densities between 10^{14} and 10^{19} cm^{-3} and of electron temperatures between 1000 and 175 000 K. The emitter and the perturber ion kinetic temperature may vary within the interval $(0.1-1) \times T_e$.

The Stark broadening of the N atomic line near 746 nm also depends on the electron temperature. The proper use of this line for the determination of electron density is, therefore, possible only if we know T_e . On the other hand, the dependence of the Stark broadening of the atomic O triplet line near 777 nm on T_e is very weak. Another advantage of using the atomic O triplet line is the intensity of its emission. Actually, this triplet line is the strongest atomic line that we observe in atmospheric pressure air plasma generated by the transient spark (TS) discharge studied in this paper [17]. The disadvantage is that the three individual lines in this triplet interfere with each other due to the strong Stark effect. It would be necessary to use a complicated fitting procedure to separate these lines.

There is an alternative method for the calculation of n_e , which is derived from the conductivity and dimensions

of the plasma. Recently, this method was successfully used for calculation of n_e in NRP discharge [18], and also for the conductivity measurements of femtosecond laser-plasma filaments [19]. We used this approach for the calculation of time evolution of n_e in the TS discharge [20, 21]. The plasma conductivity was calculated using oscilloscopic measurements, while the plasma dimensions were obtained by time-resolved imaging using a high-speed iCCD camera. In previous study [21], we have already compared the electron density estimated from the plasma conductivity and calculated from FWHA of the Stark broadened H_α line. In this paper, we compare the electron density estimated from the plasma conductivity with n_e calculated from the Stark broadening of H_α line, N line at 746 nm, and O triplet line near 777 nm. Besides the FWHA, we used also FWHM of the H_α line to calculate n_e . Reasonable agreement was obtained for $T_e = 10\,000 \text{ K}$. This electron temperature was also used to calculate n_e from the FWHM of the N line. Concerning the O triplet line, instead of using a fitting procedure for the separation of three individual lines, we tested the possibility of deriving n_e by comparing experimental and simulated spectra generated by Specpair software [9, 22].

1.1. Transient spark

Thanks to their high reactivity, atmospheric pressure plasmas have been tested for many potential applications, including bio-decontamination, surface processing, exhaust gas cleaning, and plasma assisted combustion [23–28]. The broad span of possible applications with different demands on the plasma characteristics implies that there is a large number of electrical discharges being used for the plasma generation. Besides established types of discharges, such as streamer corona [29] or dielectric barrier discharge (DBD) [30–32], new types of discharges or new types of reactors are still being developed and studied [33–35]. One of them is a DC driven self-pulsing discharge named TS [20, 36–39], which has already been successfully tested for several biological and environmental applications [40–42]. TS has been described relatively recently, but its concept is similar to the prevented spark studied by Marode *et al* in the late 1970s [43–45].

The TS is a filamentary streamer-to-spark transition discharge that is typically generated in a point-to-plane geometry with the electrode's gap $\sim 0.5-1 \text{ cm}$ (see figure 1). The TS is initiated by a streamer (time $\sim 0 \text{ ns}$ in figure 2), which transforms to a short ($\sim 10-100 \text{ ns}$) spark current pulse (time $\sim 100-200 \text{ ns}$ in figure 2). The streamer and the spark are two major phases of the TS discharge, responsible for two current pulses characteristic for the TS current waveforms (figure 2). Thanks to the short spark current pulse duration, the TS pulses generate highly reactive non-equilibrium plasma that can be maintained at relatively low energy conditions (up to 1 mJ/pulse) [20]. The short duration of the TS spark current phase results from the small amount of energy stored in the capacity C being discharged ($\sim 10-40 \text{ pF}$).

The discharging capacity C is composed of several components (internal capacity of the discharge chamber C_{int} , capacity of the high voltage (HV) cable C_{cable} between the

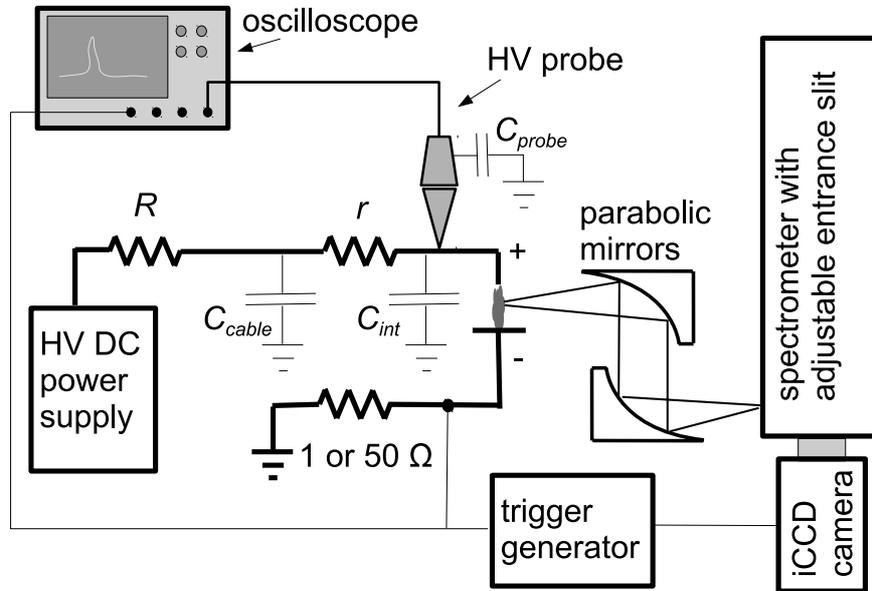


Figure 1. Simplified schematic of the experimental set-up generating the TS discharge.

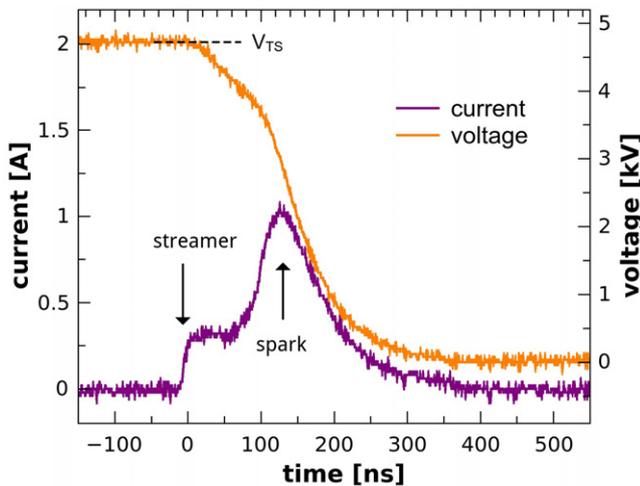


Figure 2. Typical waveforms of TS, $f \approx 6$ kHz, $C = 32 \pm 4$ pF, $d = 5$ mm.

ballast resistor R and the electrode, and the capacity of the HV probe $C_{HV} = 3$ pF). When C is discharged, the current, which is approximately given by

$$I(t) \approx -C \times \frac{dV(t)}{dt}, \quad (1)$$

reaches a high value (~ 1 A) and the voltage on the needle electrode drops to almost zero (figure 2). Then, during the quenched phase, C is recharged by a growing potential V on the stressed electrode. As soon as V reaches the characteristic TS breakdown voltage V_{TS} , a new TS pulse appears. TS generation is thus based on the charging and re-charging of capacity C . A characteristic repetition frequency f of this process is of the order of several kHz, and it can be controlled by the generator voltage V_g . The control of TS by V_g and other external circuit parameters was recently described in detail [20]. A more accurate version of equation (1), which takes into account the

influence of the ballast resistors R and r , was also provided therein.

Analysis of the electric circuit representing the TS described in [20] has enabled us to derive the plasma resistance R_p from the measured values of current and voltage waveforms. From R_p , we estimated the plasma conductivity σ_p using the equation:

$$\sigma_p = \frac{d}{R_p A} = \frac{4d}{\pi R_p D_p^2} \quad (2)$$

where d is the gap length, A and D_p are the cross-sectional area and diameter of the discharge channel, respectively. The electron density is related to the plasma conductivity σ_p by

$$n_e = \frac{\sigma_p m_e \nu_N}{e^2}. \quad (3)$$

Here e and m_e are the electron charge and mass, respectively, and ν_N is the electron-heavy particles collision frequency.

Besides the voltage and current waveform, we thus need to know D_p and ν_N to use this method to estimate n_e . In order to estimate D_p , we assumed that the discharge diameter can be well defined by the volume from which a light emission can be observed. We therefore performed a set of experiments of the TS imaging by iCCD camera. In the first approximation, we attributed the thickness of the illuminated area in the image to the plasma diameter. At low TS repetition frequencies (below 4 kHz), we observed shrinking of the discharge channel diameter during the streamer-to-spark transition from $\sim 300 \mu\text{m}$ in the streamer phase, down to less than $\sim 100 \mu\text{m}$ in the spark phase. This behavior is in agreement with the calculations of Naidis [46]. For the estimation of n_e , we used an average value $200 \mu\text{m}$ for all phases of the TS discharge at all repetition frequencies.

In order to estimate ν_N , we calculated ν_N in air for the gas temperatures T_g from 300 to 3000 K, and for reduced electric field strengths E/N from 10 to 200 Td, using our package for Monte Carlo simulation of electron dynamics [47]. We found

that within this region of T_g and E/N , the value of ν_N can vary from approximately from 2×10^{11} to $4 \times 10^{12} \text{ s}^{-1}$. We used a constant value 10^{12} s^{-1} for ν_N during all phases of TS. This approximation introduces an uncertainty of less than a factor of 4.

The estimated electron density during the spark phase of TS with $f < 4 \text{ kHz}$ was found to be $\sim 10^{16} \text{ cm}^{-3}$ [20]. This is high enough to induce Stark broadening of atomic emission lines. We therefore verified it experimentally: first on the H_α (656.28 nm) line, and next on the atomic lines of N (746 nm) and O (777 nm) to calculate n_e (section 3.1). We obtained good agreement between the electron densities calculated from these three different lines. Although we have used this measured n_e to verify the estimate of n_e from the plasma conductivity presented in our previous work [20], we found quite a significant disagreement. We therefore tried to find out how to improve the initial estimate of n_e presented in [20] (section 3.2). We mainly focused on the two major sources of the uncertainties in the estimate of n_e from the plasma conductivity, which are determination of the plasma diameter and the electron collision frequency. We performed additional TS imaging experiments with better analysis of the obtained images. With regard to the electron collision frequency, we tried to include the influence of the collisions with ions. Finally, we obtained much better agreement between the estimated and measured electron densities.

2. Experimental setup

Figure 1 shows a simplified schematic of the experimental set-up. Experiments were carried out at room temperature in atmospheric pressure air with a gas flow perpendicular to the discharge channel with a velocity of $\sim 0.2 \text{ m s}^{-1}$. A stainless-steel needle was used as a HV electrode opposite to a grounded planar copper electrode. The distance between electrodes d varied from 4 to 6 mm.

A DC HV power supply connected via a series resistor R limiting the total current was used to generate a positive TS discharge. The value of R varied from 3.5 to 9.84 M Ω . An additional small resistor $r = 1 \text{ k}\Omega$ was attached directly to the HV electrode, separating it thus from a HV cable connecting it with the resistor R (figure 1). The purpose of adding r was to eliminate the oscillations of electric signals caused by internal inductances of the HV cable and of a grounding wire. The discharge voltage was measured by two 100 M Ω HV probes (Tektronix P6015A) at both ends of the resistor r . The currents at the grounded electrode were measured on a 50 Ω or 1 Ω resistor shunt. All of the current and HV signals were linked to the 200 MHz digitizing oscilloscope (Tektronix TDS2024) with a sampling rate of up to 2 Gs s^{-1} . For further analysis, the current and voltage signal time delay was corrected to take into account the different lengths of the BNC cables that we used.

Images of single TS pulses were taken by an intensified CCD camera (Andor Istar) with a time resolution down to 2 ns. The iCCD camera was triggered by a generator of 5 V rectangular pulses, which was triggered directly by the discharge current signal. The measurement of the discharge

current on the 50 Ω or 1 Ω resistor shunt enabled us to synchronize the acquisition of the emission, either with the beginning of the streamer (50 Ω shunt) or with the beginning of the spark (1 Ω shunt) phase of the TS. However, in both cases we were unable to acquire the initial 25 ns of the emission due to a delay caused by the trigger generator, the transmission time of the signal by BNC cables, and a camera insertion delay.

The time-resolved emission spectra were obtained using the same iCCD camera coupled to a 2 m monochromator (Carl Zeiss Jena PGS2) with resolving power 45 000, covering UV and VIS regions (200–800 nm). Here, the delay between the current signal and opening of the camera was compensated using a 10 m long optical cable (Ocean Optics P400-10-UV-VIS). The Gaussian FWHM of the instrumental broadening, measured by a He-Ne laser, changes between 0.04–0.09 nm for the entrance slit from 30 μm to 100 μm , respectively. Below 30 μm , the entrance slit cannot improve the spectral resolution because it is limited by the size of the CCD chip pixels.

3. Results and discussion

3.1. Measurement of the electron density from Stark broadening of atomic lines

Since hydrogen atoms are the most sensitive to Stark broadening, we first focused on H_α (656.28 nm) and H_β (486.13 nm) lines, despite the fact that the strongest atomic lines in the emission spectra in air are atomic lines of O and N [17]. To increase the intensity of H lines, the input ambient air was humidified by simply bubbling it through a vessel with water. Although we did not quantitatively measure the achieved humidity, it can be assumed to be a maximum of 3.17 kPa, based on the saturated vapor pressure and room temperature. The humidity was low enough to avoid significant changes of the TS properties. The emission spectra were measured with the gate time 20 ns, so the emission intensity of the observed hydrogen lines was quite weak. We, therefore, had to use H_α line instead of the H_β line that was too weak, even though we accumulated a signal from up to 5000 pulses. Longer acquisition had no practical meaning due to random instabilities of the TS discharge.

In order to avoid problems with the dependence of the FWHM of the Stark broadened H_α on T_e , we calculated n_e from the full width at the half area (FWHA) of the H_α line using the formula derived by Gigosos *et al* [16]:

$$\Delta\lambda_{\text{FWHA}}^{H_\alpha} = 0.549 \text{ nm} \times \left(\frac{n_e}{10^{23} \text{ m}^{-3}} \right)^{0.67965} \quad (4)$$

Here, $\Delta\lambda_{\text{FWHA}}^{H_\alpha}$ is the FWHA of the H_α line in nm. In order to obtain reasonable values of n_e , the FWHA must be calculated from the line profile corrected with respect to Doppler, Van der Waals and instrumental broadening. However, the minimum value of FWHM that we experimentally measured was $0.14 \pm 0.03 \text{ nm}$ (at time $\sim 150 \text{ ns}$ after the peak of the spark current pulse, $f \sim 2 \text{ kHz}$). These values are so large that Doppler broadening can be completely neglected. Even after the deconvolution of the measured line profile with the measured slit function describing our instrumental broadening,

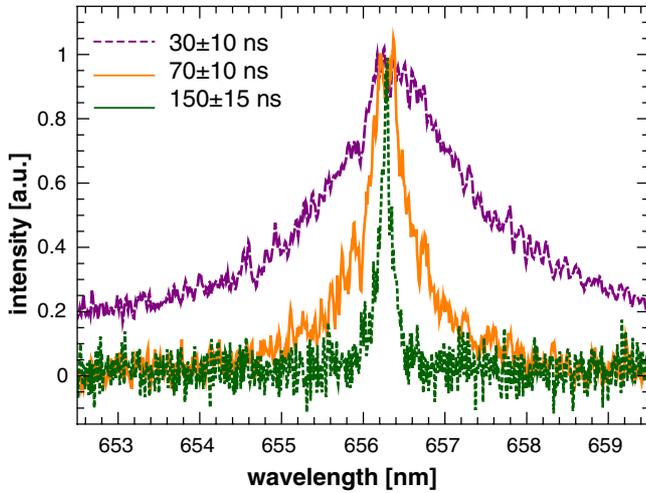


Figure 3. Normalized emission profiles of H_α line at different times after the beginning of the spark phase of the TS, $f \approx 2$ kHz.

the value of the FWHM (at 150 ns after the spark current pulse) stayed as high as ~ 0.12 nm. Thus, the influence of instrumental broadening is within the experimental uncertainty of the measured value of FWHM.

The Van der Waals broadening $\Delta\lambda_{\text{vdW}}$ can be calculated from the expression given by Djurović and Konjević [48]:

$$\Delta\lambda_{\text{vdW}} = 2.06 \times 10^{-13} \lambda_0^2 (\alpha \bar{R}^2)^{2/5} N \left(\frac{T_g}{\mu} \right)^{3/10}, \quad (5)$$

where λ_0 is the wavelength at the center of the line, α is the polarizability of the perturber, μ is the reduced mass (kg), N is the neutral number density (m^{-3}), and \bar{R}^2 is the difference between the values of the square radius of the emitting atom in the upper and lower level. The necessary polarizabilities of the perturbers in air (nitrogen and oxygen) can be found in [49] and [50], respectively. At normal conditions, for H_α line $\Delta\lambda_{\text{vdW}} = 0.1$ nm. In the spark phase of the TS, the temperature is much higher (>2000 K, see Annex 1) and the gas density is almost one order of magnitude lower than at normal conditions [46]. For these conditions, we estimated Van der Waals broadening to be less significant: $\Delta\lambda_{\text{vdW}} \sim 0.02$ nm. This would decrease the measured H_α line, broadening it to ~ 0.11 nm (150 ns after the beginning of the spark phase), which is strictly due to the Stark broadening. In the spectra obtained closer to the beginning of the current peak, where the Stark broadening was even stronger, both the instrumental and Van der Waals broadening effects can be completely neglected. Figure 3 shows the time evolutions of the normalized H_α line profiles.

The electron densities calculated from the Stark broadening of the H_α line were so high ($>10^{17} \text{ cm}^{-3}$) that even the atomic lines of N and O could be employed to calculate n_e , despite their weaker sensitivity to the Stark effect (figure 4, N line at 746 nm, figure 5, O triplet line at 777 nm). The advantage of using N or O atomic lines for the calculation of n_e from their Stark broadening is that they are present in dry air discharge. Moreover, the emission intensity is stronger and a better signal/noise ratio can be obtained without changing plasma properties by the additional humidity.

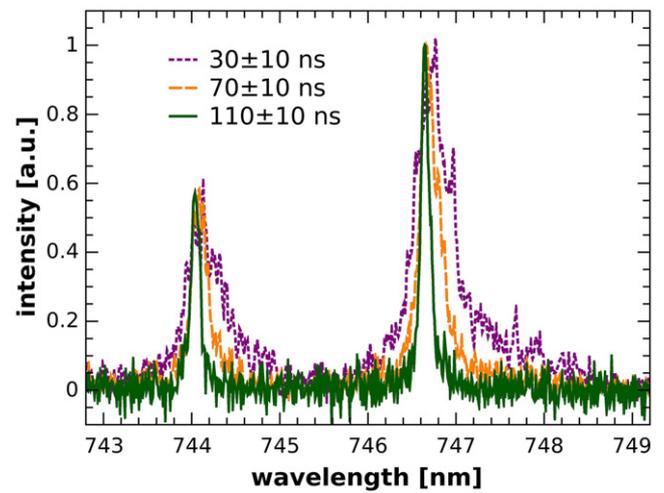


Figure 4. Normalized spectra of N around 746 nm in different times after the beginning of the spark phase of the TS, $f \approx 1$ kHz.

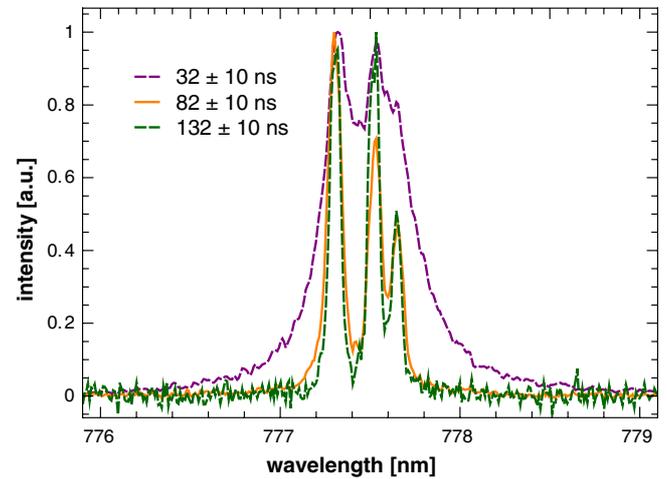


Figure 5. Normalized spectra of O triplet line around 777 nm in different times after the beginning of the spark phase of the TS, $f \approx 1$ kHz.

The calculation of n_e from the N line (746 nm) Stark broadening in NRP discharge was recently presented [13]. The whole procedure, including the handling of Van der Waals and instrumental broadening, is well described therein. The quadratic Stark effect of N was given by Griem [14], the correction introduced by Konjević [15] was used. The Van der Waals broadening of the N line at 300 K and 1 atm was calculated to be 0.04 nm [13]. At our conditions, a much lower value was obtained: $\Delta\lambda_{\text{vdW}} \sim 0.01$ nm. Besides the Stark broadening, the instrumental broadening is, therefore, the most important cause of the broadening of the measured lines. The pure Stark broadening width $\Delta\lambda_{\text{Stark}}$ of the measured lines was obtained after deconvolution by the Gaussian instrumental broadening profile.

An additional error can be introduced by the uncertainty of T_e because the $\Delta\lambda_{\text{Stark}}$ of N line depends on T_e . We could calculate T_e if we knew the reduced electric field strength E/N in the plasma channel. After the spark current pulse, E/N certainly decreases well below ~ 120 Td, which is the breakdown E/N value, most probably to a value in the range

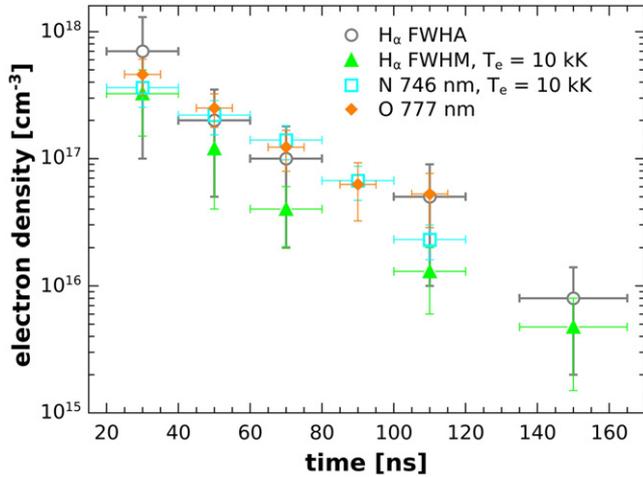


Figure 6. Comparison of electron density evolution after the beginning of the spark phase of the TS, calculated from the Stark broadening of H_α line, N line at 746 nm and O triplet near 777 nm, $f \sim 1\text{--}2\text{ kHz}$.

from 10 Td to 70 Td. Fortunately, the dependence of T_e on E/N in air is weak in this range (see Annex 2). Moreover, the dependence of Stark broadening of the N line at 746 nm on T_e is also quite weak, in the range of T_e from 0.6 to 1.2 eV ($\sim 5000\text{--}10\,000\text{ K}$) [51]. With a reasonable accuracy, we can assume $T_e = 10\,000\text{ K}$. We checked this assumption by calculating n_e from the FWHM of the H_α line with $T_e = 10\,000\text{ K}$ according to Vidal *et al* [52]. A fair agreement with n_e calculated from the FWHA of the H_α line was obtained (figure 6). The electron density obtained from the Stark broadening of the N line at 746 nm is also in a good agreement with these data (figure 6) using $T_e = 10\,000\text{ K}$.

The dependence of Stark broadening of the O triplet ($^5S^\circ, J = 2 \rightarrow ^5P, J = 1\text{--}3$) near 777 nm does not significantly depend on T_e and can be completely neglected. Another advantage of using this triplet to estimate n_e is that it is the strongest atomic line observed in VIS spectra of the TS discharge [17]. However, a disadvantage results from the overlapping of the three lines of the triplet at higher electron densities. The Stark broadening of this line is included in the Specair software package [9, 22]. We therefore used Specair to fit the experimental spectra to get n_e by changing the gas temperature, pressure, and the molar fraction of the electrons (figure 7). The advantage of using Specair is that simulated spectra can be convoluted with the measured instrumental broadening function. Doppler and Van der Waals broadenings are also included. Indeed, spectra have to be simulated under conditions relevant to experimentally measured spectra. The best results were obtained when we varied the molar fraction of electrons at $T_g = 3000\text{ K}$ and a pressure of 1 atm. However, only small changes of estimated n_e were obtained for T_g from 1000 to 5000 K and pressures from 0.5 to 10 atm.

3.2. Estimation of the electron density from the plasma resistance

Values of n_e calculated from the measured H_α line Stark broadening were compared with n_e estimated from the plasma

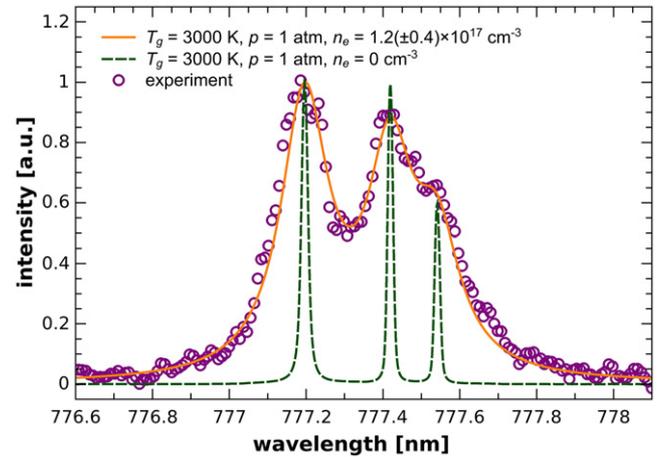


Figure 7. Experimental and Specair simulated spectra of O triplet emission line, $f \approx 2\text{ kHz}$, $\sim 70\text{ ns}$ after the rising slope of the spark pulse.

resistance calculation (formula (2) and (3)). It was found that the n_e measured from the Stark broadening is at least one order of magnitude higher than the initial estimate presented in [20]. The estimation of n_e from R_p brings forth some uncertainties from several sources. In addition to the uncertainty of R_p depending on the measured voltage and current, the discharge channel diameter D_p , and the collision frequency ν_N are major sources of uncertainty in the estimation of n_e [20]. In the first step, we tested if the disagreement between the measured and estimated n_e can be resolved by more accurate estimates of the plasma diameter, which enters the cross-sectional area A of the plasma channel in formula (3) as a square.

For the estimation of n_e , we initially used an average value of the discharge diameter $D_p = 200\ \mu\text{m}$ for all phases of the TS discharge. For a more accurate approximation of D_p , we performed additional time-resolved imaging of the TS discharge at different repetition frequencies. The aim was to obtain the time evolution of D_p during the evolution of the TS discharge. When we triggered the iCCD camera with a streamer current (measured on the $50\ \Omega$ shunt) we imaged either the whole pulse (gate time $0.5\text{--}2\ \mu\text{s}$) or the streamer only (gate time $25\text{--}150\text{ ns}$). When we triggered with a spark current (measured on the $1\ \Omega$ shunt) we imaged the spark phase only (gate time $25\text{--}500\text{ ns}$). The beginning of the iCCD acquisition always started $\sim 30\text{ ns}$ after the rising slope of the current signal due to the camera insertion delay and other delays in the circuit.

At low TS repetition frequencies (below 4 kHz) the streamer-to-spark transition phase is quite long, from a few hundred ns up to a few μs [37]. We therefore could not continuously follow the evolution of the discharge channel diameter from the beginning of the streamer until the end of the emission of the spark phase. In order to obtain D_p , we had to take an image of a single pulse. With a gate width of 25 ns we were able to determine D_p with a reasonable accuracy only for $\sim 100\text{ ns}$ from the beginning of the streamer and for $\sim 100\text{ ns}$ from the beginning of the spark phase. During these periods, we observed no significant changes in the D_p : neither after the streamer nor after the spark. On the other hand, we can compare the diameter of the discharge channel of the streamer

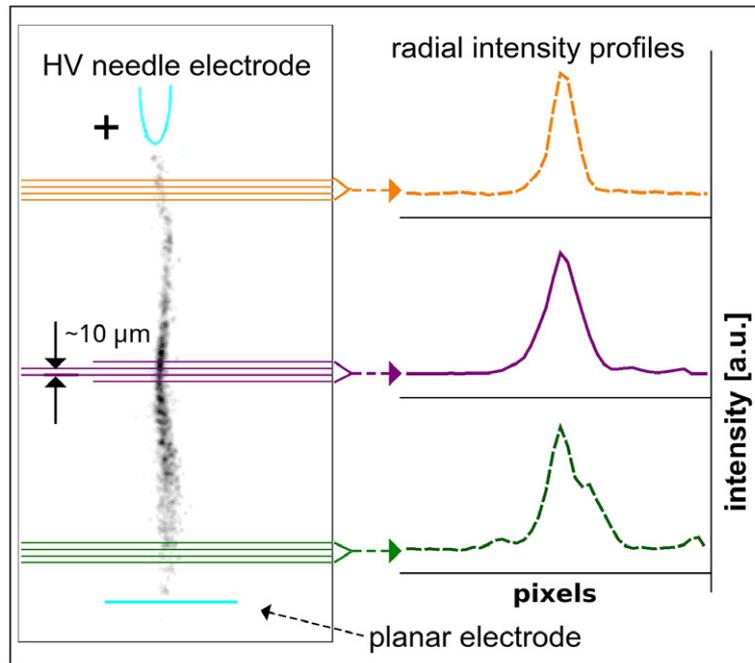


Figure 8. Image of a single TS pulse taken by an iCCD camera, 25 ns time resolution, $f \approx 2$ kHz, spark phase, inverted colors. Radial intensity profiles at three different positions are shown for illustration.

and the spark phase. We can see a shrinking of the discharge channel diameter from $\sim 300 \mu\text{m}$ in the streamer phase down to less than $\sim 100 \mu\text{m}$ in the spark phase. These numbers represent the thickness of the illuminated area in the image of the plasma channel.

For a more accurate approximation of D_p , we used the FWHM of the spectrally unresolved radial intensity profile of the plasma channel. Instead of averaging over several pulses, we could improve the obtained radial emission profiles by summing the profiles from several rows on the iCCD chip (figure 8). After the Abel inversion, we found that the diameter of the streamer was $\sim 150 \pm 40 \mu\text{m}$. This agrees with the results of Gibert *et al* [53] or Van Veldhuizen *et al* [54], who also applied optical emission measurement.

The subsequent spark phase channel was found to be narrower (for $f < 4$ kHz): less than $100 \mu\text{m}$. The FWHM of the radial emission profile of the spark phase after the Abel inversion is $\sim 50 \pm 20 \mu\text{m}$. Although it is slightly expanded near the planar electrode (see figures 8 and 9), we used the typical value for the region near the needle electrode, where we also measured the emission spectra of the H_α line. Finally, the measured n_e from the Stark broadening of H_α line agreed well with the estimate of n_e from the plasma resistance (figure 10), except for the first data point (30 ns after the beginning of the spark current pulse).

At higher TS frequencies (> 4 kHz), the streamer-to-spark transition time in the TS decreases to only ~ 100 ns [37] and we were able to observe the entire evolution of the discharge channel from the beginning of the streamer until the end of the spark. We found out that the contraction of the discharge channel during the spark phase was much weaker, or there was none. Therefore, at higher f , the approximation of D_p by a single value ($\sim 150 \pm 40 \mu\text{m}$) is reasonable and a good agreement of the measured n_e from broadening of H_α line with

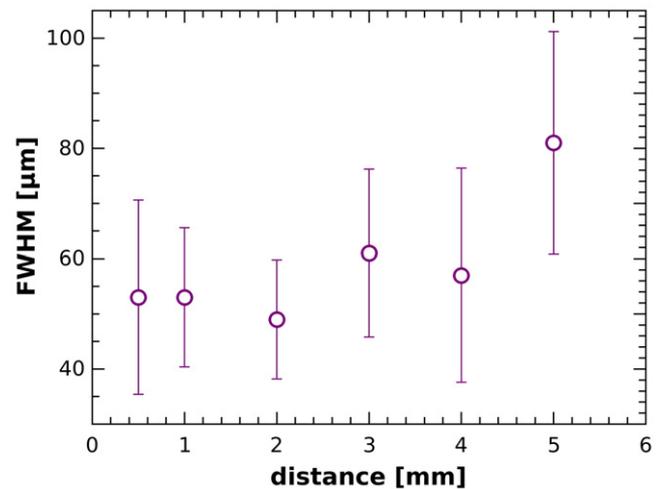


Figure 9. FWHM of the radial intensity profiles of single TS spark pulses as a function of the gap distance from the HV point electrode, after the Abel inversion, $f \approx 2$ kHz.

the estimate of n_e from the plasma resistance was obtained using this approximation (figure 11).

For further improvement of the n_e estimation from the plasma resistance we focused on the collision frequency of the electrons. Based on H_α line Stark broadening, the electron density during the TS spark current pulse is so high that the plasma is highly ionized. In order to obtain a better agreement between the estimated and measured n_e shortly after the spark current peak, it is necessary to include the collision of electrons with ions to calculate the overall collision frequency of electrons ν_C [55]:

$$\nu_C = \nu_N + n_e v \sigma_{\text{Coul}}(n_e, T_e), \quad (6)$$

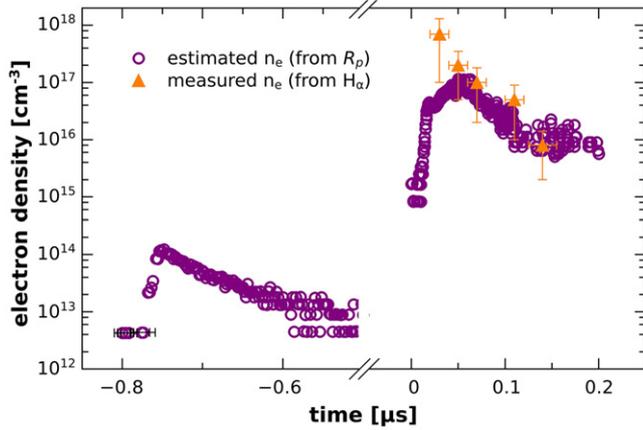


Figure 10. Electron density during the streamer and the spark phase of the TS pulse in μs time scale, estimated from the plasma resistance and measured by H_α (FWHA) Stark broadening, $f \approx 2$ kHz, $C = 32 \pm 4$ pF, and $d = 5$ mm.

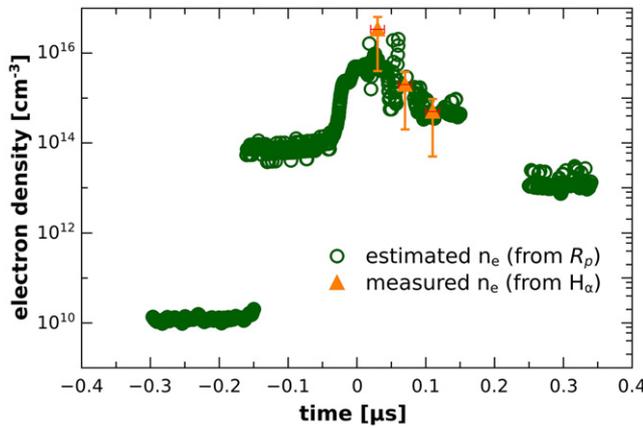


Figure 11. Electron density during the TS pulse, estimated from the plasma resistance and measured by H_α (FWHA) Stark broadening, $f \approx 6$ kHz, $C = 32 \pm 4$ pF, and $d = 5$ mm.

where v is the thermal velocity of electrons, and σ_{Coul} is the cross section of electron–ion collisions dominated by Coulomb forces. The expression for σ_{Coul} can be also found in [55]. The problem is that the v_C depends on both T_e and n_e in strongly ionized plasma, and the influence of T_e dominates. For this reason, the method of estimating n_e from R_p is not suitable for strongly ionized plasma. We can only say that the estimate of n_e from R_p is underestimated during the high current spark phase of TS.

In order to quantify the influence of electron–ion collisions, we calculated a correction factor that has to be used to multiply n_e calculated without the electron–ion collisions included. We expressed v_C as a function of electron–neutral collision frequency ν_N ($=10^{12} \text{ s}^{-1}$) and a correction factor χ depending on the electron density and temperature:

$$v_C = \nu_N \times \chi(n_e, T_e), \quad (7)$$

The correction factor χ increases with growing n_e and decreasing T_e (figure 12). The resulting error of n_e calculated using ν_N must, therefore, be the highest right after the end of the spark pulse where n_e is still very high ($>10^{17} \text{ cm}^{-3}$),

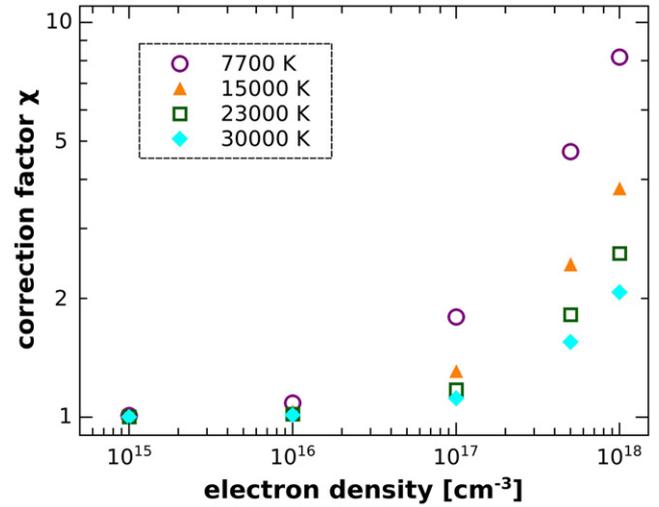


Figure 12. Correction factor for the calculation of electron collision frequency including electron–ion collisions, as a function of electron density and electron temperature.

but the electron temperature decreases to $\sim 10\,000$ K. For $n_e = 5 \times 10^{17} \text{ cm}^{-3}$ measured by the Stark broadening of H_α line at $f \approx 2$ kHz and $T_e \approx 10\,000$ K, we get $\chi \approx 4$. If we apply this correction factor, we would get a better agreement between the estimated and measured n_e at 30 ns after the beginning of the spark current peak (figure 10). Later, both n_e and the influence of electron–ion collisions decreases, and the approximation based on ν_N is valid again.

With increasing repetition frequency, the TS current pulses become smaller and broader [37]. The electron density of n_e in the spark phase, therefore, also decreases with the increasing f . The maximum n_e reaches $\sim 10^{16} \text{ cm}^{-3}$ at $f \approx 6$ kHz (figure 11). We assume that the ionization degree is low and the estimate of n_e from R_p is closer to the real value than at $f < 4$ kHz, without the electron–ion collisions included.

However, the agreement between these two methods could be to some degree accidental. The diameter obtained from the spectrally unresolved emission need not necessarily be identical to the real ‘electrical’ plasma diameter. Moreover, the emission profiles from which D_p was derived were Abel inverted, while the atomic lines were obtained from the line-in-sight integrated emission. The line-in-sight integrated emission scan is dominated by emission from the central plasma core. Thus, the line-of-sight measurement provides, to a good approximation, the n_e at the centerline of the plasma [9]. As a result, the n_e from the Stark broadening should be higher than the n_e derived from the plasma conductivity. This could also partially explain the big discrepancy observed at lower TS frequencies shortly after the beginning of the spark phase of TS, although there are other possible explanations, as discussed in the next paragraphs.

The strong degree of ionization at the beginning of the spark phase of TS disqualifies not only the method based on σ_p but it can also influence n_e obtained from the Stark broadening of atomic lines. A proper subtraction of the continuum background is important to get the correct FWHM of these lines. We approximated the background subtracted

from these lines by linear functions. This could introduce some additional inaccuracy determining FWHM (or FWHA), particularly in the early time of the spark phase of the TS, where the H_α line is significantly broadened and the linear approximation of the background continuum could be less accurate.

Finally, another source of uncertainty in n_e , as measured from the Stark effect, could be due to the space charge field F_c , especially at the beginning of the spark phase when the conductivity is still low. The F_c also induces the Stark effect and influences the line width [56] if F_c is not negligible compared to the microfields F_o from the ions surrounding excited H atoms, which is called Holtsmark field [57]. Reference [56] shows how the line profile may change with the parameter $p_c = F_c/F_o$ and with the electron temperature T_e . Namely, a table is given for H_α and $n_e = 10^{17} \text{ cm}^{-3}$.

At the beginning of the spark phase of TS at lower frequencies, the F_c can be as high as 14 kV cm^{-1} (breakdown voltage $\sim 7 \text{ kV}$, gap 5 mm). The Holtsmark field F_o in V cm^{-1} is given by [57]:

$$F_o = 3.75 \times 10^{-7} n_i^{2/3}, \quad (8)$$

where n_i is the density of ions in cm^{-3} . If $n_i \approx n_e = 10^{17} \text{ cm}^{-3}$, $F_o \approx 80 \text{ kV cm}^{-1}$, and the parameter $p_c \approx 0.175$. Referring to [56], it seems that the influence of F_c is minor but not negligible. This effect could thus slightly contribute to the overestimation of n_e obtained from the Stark broadening (e.g. 30 ns after the beginning of the spark current pulse, figure 10). However, 30 ns after the beginning of the spark current pulse, the conductivity is already much higher than at the beginning of the spark phase (current rising slope), the voltage drops to a low value and F_c will not be as high as 14 kV cm^{-1} . It is probably much lower and so probably negligible compared to F_o . This is certainly true in the later phase after the spark current pulse, which makes the n_e measured from the Stark broadening more realistic.

4. Conclusions

TS, which is a DC-driven self-pulsing discharge, was investigated. TS represents a repetitive streamer-to-spark transition discharge of very short pulse duration (~ 10 – 100 ns) with a very limited energy, so that the generated plasma stays out of equilibrium. This discharge can be maintained at low energy conditions (up to 1 mJ/pulse) by an appropriate choice of the resistances and capacities in the electrical circuit. Its frequency can be controlled by the applied voltage. The chemical activity of the TS is comparable with the nanosecond repetitive pulsed discharges, its advantages include the ease of the DC operation and no need for special and expensive high voltage pulsers with high repetitive frequency and nanosecond rise-times. An electron density n_e as high as 10^{17} cm^{-3} in the spark phase of the TS at repetition frequency $\sim 2 \text{ kHz}$ can be achieved.

We characterized the evolution of n_e in the TS discharge using two methods: the n_e was calculated from the plasma resistance and from the Stark broadening of atomic lines

measured by time resolved OES. Finally, good agreement between these two methods was obtained. However, an accurate estimate of the discharge channel diameter D_p is critical for the calculation of n_e from the plasma resistance. A fast iCCD camera was used for time-resolved imaging of the TS discharge to obtain D_p , which is defined as a full width at the half maximum of the radial intensity profile of the discharge channel after the Abel inversion. Different values of D_p had to be used for the streamer ($\sim 150 \mu\text{m}$) and the spark ($\sim 50 \mu\text{m}$) phases of the TS discharge at lower repetition frequencies ($< 4 \text{ kHz}$) because the D_p has contracted in the spark phase. At higher frequencies, no discharge channel contraction occurred during the streamer-to-spark transition phase and a single value of D_p typical for the streamer could be used to calculate n_e .

The estimate of n_e from the plasma resistance is less sensitive to the collision frequency of electrons. With a reasonable accuracy, a single value 10^{12} s^{-1} can be used for a weakly ionized non-equilibrium air plasma for the gas temperature T_g from 300 to 3000 K and for the reduced electric field strength E/N from 10 to 200 Td. However, this method is not suitable for a strongly ionized plasma where collisions of electrons with charged particles cannot be neglected. This defines the upper limit of this method. In our case, we can use it only for $n_e < 10^{17} \text{ cm}^{-3}$. The lower detection limit of this method depends mostly on the accuracy of the current measurement, from which the plasma resistance is calculated. For the current measured on a 50Ω shunt, our detection limit is 10^{12} – 10^{13} cm^{-3} . This limit is lower than using Stark broadening of atomic lines.

The detection limit of the method based on the Stark broadening of atomic lines is given by several parameters. The Stark broadening must surpass other broadening mechanisms (instrumental, van der Waals, and Doppler), and it also depends on the intensity of the emission signal. The lowest electron density we have measured from the Stark broadening was slightly below 10^{15} cm^{-3} , using full width at the half area FWHA of the H_α line. We could, therefore, calculate n_e from the Stark broadening of the atomic lines only during the spark phase of TS, while the plasma resistance method enabled us to also calculate n_e during the streamer phase. The advantage of the Stark broadening method is that it is also valid in strongly ionized plasma. The FWHA of the H_α line can be theoretically used for n_e up to 10^{19} cm^{-3} [16].

We measured the Stark broadening of three different lines: H_α line, N line at 746 nm and O triplet line at 777 nm. We obtained the same n_e from all of them within the experimental uncertainty. The use of each of these lines has a number of advantages and disadvantages. The H_α line is the most sensitive to the Stark effect, it should also have the lowest detection limit for n_e . When using the FWHA of the H_α line for the calculation of n_e , we avoid the dependence of the Stark effect on the electron temperature T_e . On the other hand, the intensity of the H_α line in humid air plasma is typically much weaker than the intensity of N and O lines, it is not available at all in dry air.

The most suitable atomic lines for the calculation of n_e in dry air are atomic lines of N and O. The method is relatively straightforward for N line at 746 nm if T_e is known. We found

that, for the spark phase of TS shortly after the spark current pulse, $T_e = 10\,000$ K can be used with a reasonable accuracy. The influence of T_e on the broadening of the O triplet line at 777 nm is weak and can be neglected. The disadvantage of using O triplet line results from the mutual overlapping of its three lines at higher electron densities. We showed that it is possible to use Specair software [9, 22] to fit the experimental spectra to get n_e from this triplet line. The advantage of using Specair is that simulated spectra can be convoluted with the measured instrumental broadening function. Doppler and Van der Waals broadenings can also be included.

The measured evolution of n_e during different phases of the TS discharge is useful for its better understanding and easier adaptation for specific applications. It also helps us to assess the reactivity of the plasma generated by the TS. The decrease of maximum n_e with the increasing TS repetition frequency can be explained by the decrease of the reactivity of generated plasma. However, it is necessary to perform kinetic modeling of TS in air to confirm this assumption. For this purpose, we are developing a kinetic model of TS based on ZDPlasKin package [58]. The goal is to mimic the evolution of the reduced electric field strength E/N during all phases of TS, so that the calculated electron densities agree with experimental data presented in this paper. Once this goal is fulfilled, a validated kinetic model of TS will help us to further understand the induced plasma chemistry.

Annexes

Annex 1—Gas temperature measurement from N_2 emission spectra

We used the time-resolved spectra of the N_2 2nd ($C^3\Pi_u - B^3\Pi_g$) positive system to determine the gas temperature T_g , assuming that it approximately equals the rotational temperature of excited $N_2(C^3\Pi_u)$ species. This rotational temperature was inferred from the spectra using SPECAIR package [9, 22]. The ICCD camera was synchronized with the beginning of the spark pulse—by the current signal measured on 1 Ω shunt.

Previously we measured changes of the temperature at the beginning of the streamer and a subsequent evolution of the temperature during the streamer-to-spark transition phase [37]. The steady-state gas temperature, measured at the beginning of the streamers initiating the TS, increased from an initial value of ~ 300 K only up to ~ 550 K at repetition frequency 10 kHz. After the streamer, an increase of the temperature increased up to ~ 1000 K, as measured at the beginning of the spark phase. A further increase of the gas temperature up to ~ 2500 K was observed at $f \approx 6$ kHz.

For the purposes of the study presented in this paper, we focused on the gas temperature in the spark phase of TS at various repetition frequencies. Figure 13 shows the highest temperature derived from the time-resolved spectra of the N_2 2nd ($C^3\Pi_u - B^3\Pi_g$) positive system as a function of f , with time resolution 20 ns. The uncertainty in these data is quite high at lower TS repetition frequencies, despite the accumulation over 1000 pulses. The $N_2(C^3\Pi_u)$ species

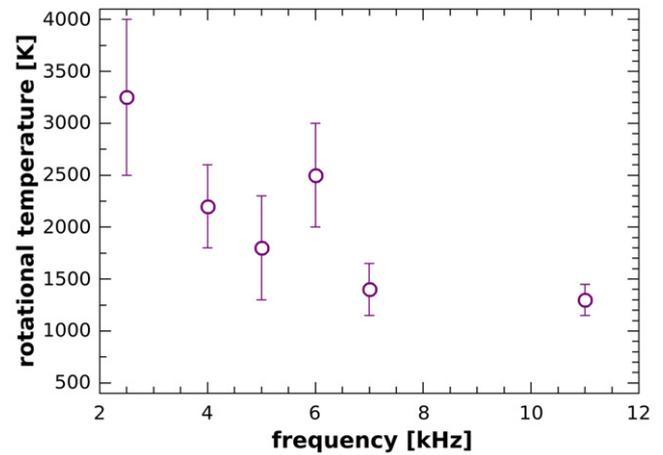


Figure 13. The highest temperature during the spark phase of TS, approximated by the rotational temperature derived from the time-resolved spectra of the N_2 2nd positive system ($C^3\Pi_u - B^3\Pi_g$) as a function of f , with time resolution 20 ns.

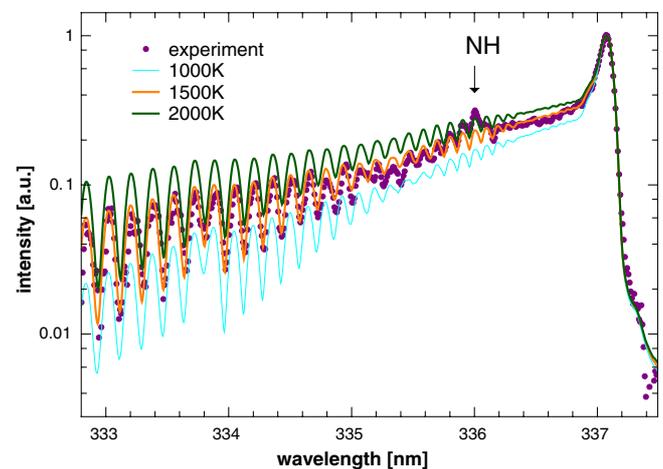


Figure 14. Experimental and Specair simulated spectra of 0-0 transition of N_2 2nd positive system, $f \approx 2$ kHz, ~ 30 ns after the beginning of the spark pulse (not the spectrum from which the highest temperature at $f \approx 2$ kHz was determined).

are produced mainly during the streamer phase of the TS discharge [37] and their life time is so short that they decay before the onset of the spark phase of the TS at lower repetition frequencies. At $f > 3$ kHz, with much shorter streamer-to-spark transition phase, during the spark phase, we still observed quite a strong emission from $N_2(C^3\Pi_u)$ generated during the streamer. At lower TS frequencies, we depend on a small amount of $N_2(C^3\Pi_u)$ species that are generated during the spark phase. Moreover, there is interference of the NH emission with the strongest emission band of the $N_2(C^3\Pi_u)$ species (0-0 vibrational transition, figure 14). The use of other vibrational transition bands does not significantly improve the uncertainty of the calculated temperature, which is due to a weaker signal.

Annex 2—Monte Carlo simulations of electron dynamics

The calculation of the mean electron energy and their temperature T_e requires a knowledge of the electron

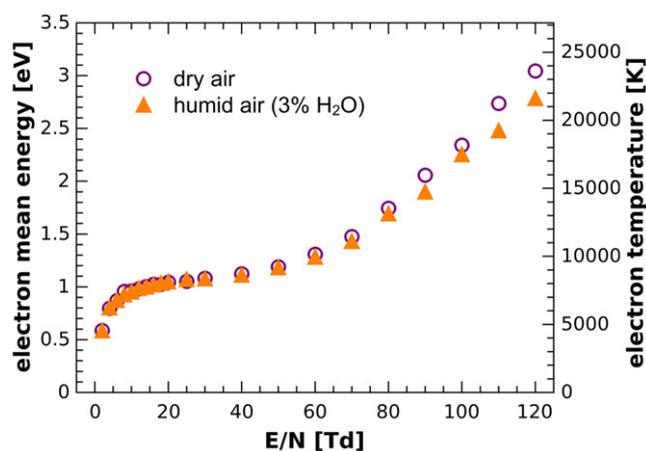


Figure 15. Electron mean energy and electron temperature in dry and humid air (3% H₂O) as functions of the reduced electric field strength E/N .

energy distribution function (EEDF). In non-equilibrium cold plasmas, EEDFs may have strongly non-Maxwellian shapes, but they satisfy the Boltzmann equation. Thus, one way to obtain EEDFs is to solve simplified versions of the Boltzmann equation numerically. The second approach is to use Monte Carlo (MC) methods. We use an open source software program named ‘Web-EEDF’ for the calculation of EEDF [47, 59, 60], which is based on the algorithm presented by Tas *et al* [61]. ‘Web-EEDF’ derives the EEDF from the MC simulation of electron dynamics in constant electric fields in gas mixtures. The reliability of ‘Web-EEDF’ was checked by comparison with the data found in literature [59, 60].

Besides the composition of the gas, the major factor determining the EEDF is the reduced electric field strength (E/N). The problem is that we do not really know the value of E/N in the plasma channel generated by the TS discharge. However, after the spark current pulse, E/N certainly decreases well below ~ 120 Td, which is the breakdown E/N value, most probably to a value in the range from 10 Td to 70 Td. Fortunately, the dependence of T_e on E/N in both humid and dry air is weak in this range (figure 15). With a reasonable accuracy, we therefore assumed that $T_e = 10\,000$ K during the period shortly after the spark pulse of the TS discharge.

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