Spatially resolved spectroscopy of a dielectric barrier discharge plasma jet for soft ionization

S.B. Olenici-Craciunescu, A. Michels, V. Horvatic*, C. Vadla*, J. Franzke

ISAS – Leibniz Institut für analytische Wissenschaften, Bunsen-Kirchhoff-Strasse 11, 44139 Dortmund; Otto-Hahn-Straße 6b, 44227 Dortmund; Albert-Einstein-Str. 9, 12489 Berlin Germany

* Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

Abstract

An atmospheric pressure microplasma ionization source based on a dielectric barrier discharge with a helium plasma cone outside the electrode region has been developed for liquid chromatography/mass spectrometry and as ionization source for ion mobility spectrometry. It turned out that dielectric barrier discharge ionization could be regarded as a soft ionization technique characterized by only minor fragmentation similar to APCI. Mainly protonated molecules were detected. In order to characterize the soft ionization mechanism spatially resolved OES measurements of the He, N$_2^+$ and N$_2$ spectral line intensities were performed. The obtained mapping of the plasma jet shows clearly different number density distributions of relevant excited species and indicates the positions where the highest efficiency of the water ionization and the protonation process is expected. A modeling of the spatially dependent excitation energy transfer processes involving He, N$_2$^+, N$_2$ and H$_2$O is presented and compared with the experimental findings.

1. Introduction

The coupling of liquid chromatography and mass spectrometry (LC/MS) has been established as one of the most powerful tools in analytical chemistry, especially in biomedical and biochemical research, and has resulted in important advances. This is the result of extensive basic research on atmospheric pressure ionization (API) techniques, which today offer a robust way to couple LC to MS. The main API techniques are electrospray ionization (ESI) [1,2] atmospheric pressure chemical ionization (APCI) [3,4] and less
frequently applied atmospheric pressure photoionization (APPI) [5,6]. ESI, APCI, and APPI differ in their ionization process and their applicability [7]. ESI revolutionized biochemical research by offering a highly sensitive method for the analysis of large biomolecules [8]. It has been widely used also for smaller polar organic molecules, and it is the most widely used API technique today. The ionization in an ESI interface is considered primarily as liquid-phase ionization technique: ions preformed in a solution are desorbed or evaporated to the gas phase and can subsequently be mass analyzed. The ionization efficiency tends to be poor for more nonpolar compounds. For these, APCI and APPI are more suitable.

The ionization conditions in APCI are considered to be somewhat “harder” than those in ESI [9]. The ionization in APCI is understood to be primarily based on gas-phase ion-molecule reactions between analyte molecules and a solvent-based reagent gas, generated by a series of ion-molecule reactions initiated by electrons from the corona discharge needle. As an alternative ionization technique to APCI-MS for nonpolar compounds, APPI has been introduced [5,6]. The APPI interface can be considered as a modified APCI source, with the corona discharge being replaced by a gas discharge lamp except that other ionization mechanisms will take place. In APCI, the initial ionization by corona discharge takes place in a very small volume near the needle tip. Therefore, it can be expected that an increased plasma volume results in a larger fraction of ionized analytes, leading to improved sensitivity. A dielectric barrier discharge (DBD) can be used to generate low-temperature plasmas at atmospheric pressure [10,11]. The DBD is typically formed between two electrodes, with at least one dielectric layer which separates the electrode from the plasma. The DBD plasmas are suitable for the atomization of volatile species [12-14]. Furthermore, different geometrical arrangements have also served as an ionization source for ambient MS [15-18] and ion mobility spectrometry (IMS) [19-21]. The miniaturized plasma was found to be a stable and efficient ionization source and was, for this reason, ideal for ion mobility spectrometry. The sensitivity, selectivity, and resolution of the plasma IMS were significantly higher than those of a comparable β-radiation IMS. Furthermore the high ionization yield
of the plasma IMS enables variation of the electric field in the drift region and use of shorter opening time of the shutter grid; both approaches result in an increase of selectivity. A further advantage of the plasma IMS is the variable sensitivity achieved by variation of the He flow-rate and of the high voltage of the plasma. Overall, a miniaturized plasma as ionization source for ion mobility spectrometry is a more than adequate alternative to radioactive and other ionization sources.

Furthermore, DBD offers a new approach for efficient ionization for LC/MS applications [22]. A dielectric barrier discharge ionization (DBDI) was implemented into a commercial API interface for LC/MS applications. A heterogeneous compound library was investigated by DBDI to illustrate the potential use of the miniaturized plasma as an alternative ionization technique to ESI, APCI, and APPI.

Nitrogen plays an important role for soft ionization mechanisms using capillary dielectric barrier discharge [21]. In a DBD applying He as plasma gas, nitrogen can be excited to the upper level of the N$_2^+$ first negative system (B $^2\Sigma_u^+$) by Penning ionization due to the He metastables. Therefore, the population of the excited upper level of N$_2^+$ first negative system (B $^2\Sigma_u^+$) cannot exceed the population density of the metastables. In order to get the most sensitive IMS or MS signals, pure He should be used. The dissociation process of water by collisions of N$_2^+$ and the protonation process of sample molecules should spatially be in the vicinity of the maximum N$_2^+$ population. Therefore a spatially resolved measurement of the soft ionization plasma jet is of special interest.

In the present work 2D spatially resolved OES measurements of the He, N$_2^+$ and N$_2$ spectral lines emitted from the axially symmetric plasma jet were performed. The obtained line intensity distributions correspond to the position-dependent number densities of relevant excited species. These distributions are clearly different and indicate the region in the plasma jet where the protonation process occurs. A cascade excitation energy transfer starting with helium metastable atoms and involving N$_2$ and H$_2$O was established and used for the modeling of line intensity distributions in the plasma jet with decreasing helium and increasing air number density. The presented modeling shows a
general agreement with the experimental findings, which in turn confirms the predicted main excitation and de-excitation paths in the investigated plasma jet.

2. Experiment and measurements

2.1 Experimental arrangement for plasma jet mapping

In the present work the plasma jet is generated by a dielectric barrier discharge. DBD is constructed using a 30 mm long glass capillary having an outer diameter of 1.2 mm and an inner diameter of 0.5 mm. One end of the capillary is the gas inlet and the other end is left in open air. Two copper disk shaped electrodes with a thickness of 1 mm surround the capillary at a distance of 10 mm one to the other. The opening through the electrodes have the same diameter as the outer capillary diameter, so they are as tight as possible on the glass to provide a good connectivity between them and the dielectric glass. The electrodes are encapsulated in Teflon plates to prevent direct arc discharges between them. The distance from the open end of the capillary to the first electrode (cathode) is approximately 2 mm. The whole construction - capillary, electrodes and connecting cables - is encapsulated in a Teflon cage.

The plasma jet is obtained using He as working gas which is provided with two different gas flow-rates $F_a = 300$ and $F_b = 1000$ ml min$^{-1}$. The electrodes are connected through isolated cables to a high voltage generator designed and built at ISAS. A function generator that provides rectangular pulses of 2 µs width modulates the signal applied on the electrodes. The corresponding values for stable plasma are 6 kV at 20 kHz.

Depending on the gas flow-rate the plasma jet has different length 10 and 20 mm for the 300 and 1000 ml min$^{-1}$, respectively.

The plasma jet mapping was performed by optical emission spectroscopy. For this purpose an USB4000 spectrometer in the visible range (300 - 956 nm) and an optical fibre 600 µm UV/VIS 300-1100 nm from Ocean Optics were used together with the software (OIIBase32). The optical arrangement used for the plasma jet mapping is presented schematically in figure 1. The top view of the plasma jet, the focusing lens ($f = 10$ mm) and the entrance of the optical fibre is depicted in the upper part. The lower part shows a vertical
section of the arrangement. Both the Teflon cage encapsulating the glass capillary and the acquiring end of the optical fibre are mounted on micrometric stages that allow three-dimensional adjustments. These parts are adjusted by means of a He-Ne laser to be on the same optical axis. The distances between the plasma jet to the lens and between the lens to the optical fibre determines object to image ratio of 1:2. Since the aperture of the optical fibre was about 0.5 mm, only the light from a thin column along the optical axis of the investigated plasma jet was detected.

![Fig. 1 Optical arrangement for plasma jet mapping](image)

The effective jet mapping was performed by translating the capillary along the x-axis in 1 mm steps. For each x position the optical fibre was shifted along the vertical axis (z) in 0.1 mm steps symmetrically with respect to the x-axis. Thus, the different parts of the jet were imaged on the optical fibre with spatial discrimination in z-direction of 0.05 mm. At each (x,z) position the spectra were acquired with 500 ms integration time. The spectra were taken at five and nine x-positions, for lower and higher gas flow-rates, respectively. The spectra were stored on laboratory PC for further analysis.

### 2.2 Measurements and results

Some results of the plasma jet mapping obtained at lower flow-rate of helium (flow-rate $F_A = 300 \text{ ml min}^{-1}$) are illustrated in Fig. 2. In that figure the intensities of two spectral lines for each of He, N$_2^+$, and N$_2$ are shown starting at the x position 0 which is the orifice of the capillary. The spectral line peak
intensities measured at particular (x, z) positions are represented by contours of constant intensity. Areas between the contours are filled with shades of gray in the range between white (intensity maxima) and black. There is a clear difference between the spatial intensity distributions regarding the type of emitting species. Helium lines exhibit intensity maximum close to the capillary orifice, where the intensities of the N$_2^+$, and N$_2$ lines are very weak. At a distance of about 2 mm from the capillary orifice both the N$_2^+$ and the N$_2$ line groups reach their maxima. With further increase of distance x, intensities of the N$_2^+$ lines decrease faster than the intensities of the N$_2$ lines.

![Fig. 2 Spatial intensity distributions of two He, N$_2^+$, and N$_2$ lines represented in two-dimensional contour plot. White areas indicate the regions of intensity maxima in the z-x plane. The measurements were performed at the flow-rate $F_A = 300$ ml min$^{-1}$ through the capillary.](image)

When the higher helium flow-rate $F_B$ of 1000 ml min$^{-1}$ is applied through the capillary barrier discharge, the general picture remains the same as given in Fig. 2. However, the regions of the N$_2^+$, and N$_2$ line intensity maxima are shifted towards larger distances from the capillary. In addition, the intensity distributions are broader than in the case of the lower He flow-rate. This effect is illustrated in Fig. 3.
Fig. 3. Two-dimensional contour plot of intensity distributions in z-x plane for He 706 nm line (upper part), \( \text{N}_2^+ \) 427 nm line (middle part) and \( \text{N}_2 \) 380 nm (lower part). White areas indicate the regions of intensity maxima. The measurements were performed the He flow-rate \( F_B = 1000 \text{ ml min}^{-1} \).

Fig. 4. Intensity distributions of the He 706 nm, the \( \text{N}_2^+ \) 427 and the \( \text{N}_2 \) 380 lines extracted from the data presented in Fig. 3. Left: Normalized radial line intensity distributions represented by measurements along the z-axis at the position \( x = 4 \text{ mm} \). Full width at half-maximum of radial intensity distributions amounts to about 0.9 mm. Right: Normalized intensity distributions along the x-axis (\( z = 0 \)) presented in semi-logarithmic plot. The size of used symbols approximately represents the experimental error bars. Full straight lines are linear fits through data at the four largest values of x.

A quantitative description of investigated spatial line intensity distributions is given in Fig. 4, where a part of the data set from Fig. 3 is extracted. The plasma jet is radially symmetric with respect to the x-axis. As one can see in
Fig. 4 (left), the radial intensity distributions of the He, N$_2^+$, and N lines, i.e. the intensities measured along the z-axis cannot be distinguished within the error bars. These distributions are governed by diffusion of excited helium atoms into surrounding atmosphere in radial direction. However, as already shown in Fig. 2 and 3, particular distributions are strongly separated in x-direction, which is governed by the helium flow-rate. The data in Fig. 4 (right) are presented in semi-logarithmic plot, where the linear fits for the largest distances indicate that all three distributions exhibit exponential decrease. In contrast to the He and N$_2^+$ lines, the N$_2$ line intensities decrease much slower.

The intensity of an optically thin spectral line is proportional to the product of the number density in the relevant upper state and the corresponding radiative transition probability. Thus, spatial intensity distributions of optically thin lines emitted by different species yield the information about position-dependent relationships between number densities in relevant upper states. In the following section, a simplified semiquantitative modeling will be applied to describe the obtained line intensity distributions.

3. Modeling

3.1 Spatial density distributions in the jet

In the present case we have a free burning helium plasma jet, which penetrates from the capillary into the air. Initially, at x=0, the helium number density $n_{\text{He}}$ has a maximum value $n_{\text{He}}(0)$ which is defined by the atmospheric pressure and plasma gas temperature. It is reasonable to assume that the x-dependence of the helium number density can be described by an exponential function:

$$n_{\text{He}}(x) = n_{\text{He}}(0) f_{\text{He}}(x) = n_{\text{He}}(0) \exp(-ax). \quad a>0 \quad (3.1)$$

Then, since the pressure is constant, the air number density distribution along the x-axis is determined by

$$n_{\text{air}}(x) = n_{\text{air}}(\infty) f_{\text{air}}(x) = n_{\text{air}}(\infty) \left[1 - \exp(-ax)\right], \quad (3.2)$$
where \( n_{\text{air}}(\infty) \) is given by the atmospheric pressure and room temperature. It is plausible that the air components (N\(_2\), O\(_2\), H\(_2\)O) obey the same normalized distribution

\[
f_{\text{comp}}(x) = f_{\text{air}}(x) = (1 - \exp(-ax)) \quad (\text{comp: } \text{N}_2, \text{O}_2, \text{H}_2\text{O}) \tag{3.3}
\]

Regarding the high-frequency pulses of the plasma generator, the plasma jet is in a quasi-stationary regime. Therefore, the spatial distribution \( f_{\text{el}}(x) \) of the electrons produced in the discharge as well as the spatial distributions of excited particles can be regarded as time independent. Furthermore, it is justified to assume that in the present case \( f_{\text{el}}(x) \) exhibits also an exponential decrease with increasing distance from the capillary orifice and we postulate here that

\[
f_{\text{el}}(x) = \exp(-bx), \quad b > 0 \tag{3.4}
\]

It should be emphasized that, primarily due to temperature difference between plasma and air, the coefficients \( a \) and \( b \) are functions of position \( x \) too. However, since the gas temperature of the plasma jet is slightly higher than the room temperature one can approximately take both coefficients to be constant.

### 3.2. Excitation energy transfer processes involving He, N\(_2\), and H\(_2\)O

Modeling of line intensity distributions in our experiment, governed by the corresponding number densities in excited states, was performed by using a strongly simplified term scheme. In this scheme (see Fig. 5) each of the relevant states of the involved particles (He, N\(_2^+\), N\(_2\), (H\(_2\)O\(^+\), H\(_2\)O) is represented as a single state.
In the first step, helium atoms are excited due to collisions with fast electrons produced in the discharge (electron impact excitation process):

\[ \text{He}(0) + e_{\text{fast}}^{-} \rightarrow \text{He}^* (2) + e_{\text{slow}}^{-}, \]  

which occurs inside and partially outside of the capillary. The process (3.5) is characterized by a rate, i.e. collisional transition probability \( R_p \) (units: \( s^{-1} \)). In the next step, the metastable helium atoms are populated radiatively in the transition from the higher excited state:

\[ \text{He}^* (2) \rightarrow \text{He}^M (1) + h \nu_{21}, \]  

Among other collisional de-excitations of metastable helium atoms, in the present case Penning ionization of nitrogen molecules is an important process:
In addition, helium metastables are de-excited due to collisions with slow electrons:

$$He^M (1) + e^{-}_{\text{slow}} \rightarrow He (0) + e^{-}_{\text{fast}}$$  \hspace{1cm} (3.8)

where $R_D$ is the corresponding de-excitation rate. Radiative depopulation rates for helium metastables are very small, i.e. their radiative lifetimes are very long (order of magnitude: seconds). Nevertheless, their effective lifetimes in plasma are significantly shorter due to collisions with electrons. Therefore, the process (3.8) has to be taken into account.

The higher excited state $4_2^J$ of the ionized nitrogen molecule, populated in reaction (3.7), is de-excited in the radiative process $4_2^J \rightarrow 3_2^J$:

$$N_2^+ (4_2^J) \rightarrow N_2^+ (3_2^J) + h\nu_{43}$$  \hspace{1cm} (3.9)

The radiatively populated ground state $3_2^J$ of the ionized nitrogen molecule is depopulated in a series of recombination processes determined by rates $R_{3jJ}$:

$$N_2^+ (3_2^J) + e^- \rightarrow N_2 (j_2^J) + h\nu^J \hspace{1cm} (j = 2', 1', 0')$$  \hspace{1cm} (3.10)

In addition, ionized nitrogen molecule in the state $3_2^J$ can be depopulated in collisions with $H_2O$ molecules:

$$N_2^+ (3_2^J) + H_2O \rightarrow N_2 (0_2^J) + (H_2O)^+ + \Delta E$$  \hspace{1cm} (3.11)

where the energy difference $\Delta E$ between ionization energy of $N_2$ and $H_2O$ is transferred to the kinetic energy of collision products.

In the present experiment, the production of ionized water is detected by appearance of strong $N_2$ lines. Namely, there is a probability for the process

$$H_2O (12') + N_2 (0_2^J) \rightarrow H_2O + N_2 (2_2^J) + \Delta E$$  \hspace{1cm} (3.12)
in which the ionized water molecule transfers its potential energy to the lower relatively close lying excited state \(2'\) of the neutral nitrogen molecule. Then, in the final de-excitation step considered here, the second excited state \(2'\) of \(\text{N}_2\) is depopulated in \(2' \rightarrow i'\) radiative transitions:

\[
\text{N}_2(2') \rightarrow \text{N}_2(j') + h\nu_{2j} \quad (j = 1', 0')
\]  

(3.13)

Certainly, excited \(\text{N}_2\) molecules can be produced due to electron impact. However, under the present experimental conditions this mechanism is negligible in comparison with the process (3.13). This is indicated by the fact that in the region close to the capillary orifice the \(\text{N}_2\) lines are very weak (see Figs. 2 and 3).

Regarding the depopulation of \((\text{H}_2\text{O})^+\), besides the transfer (3.12) there is a number of collision processes involving the electrons and air components. First, one should take into account radiative recombination with electrons

\[
(\text{H}_2\text{O})^+ + e^- \rightarrow \text{H}_2\text{O} + h\nu^0
\]  

(3.14)

where the rate \(R_i^\nu\) represents a sum of all recombination rates. Without going into details at this point, we represent all other collision processes leading to the depopulation of ionized water by general expression

\[
(\text{H}_2\text{O})^+ + M_1 \rightarrow M_2 + M_3
\]  

(3.15)

Here, the \(M_1\) symbolizes either electrons or particular air component, while \(M_2\) and \(M_3\) label corresponding collision products. \(M_1\) could be an organic molecule when offered as reaction partner and the protonation can be initiated.

In principle, in the presented cascade one can consider the direct excitation energy transfer \(N_2(3') \rightarrow N_2(2')\) in collisions with \((\text{H}_2\text{O})^+\), where water either remains ionized or releases its energy in transition \((\text{H}_2\text{O})^+ \rightarrow \text{H}_2\text{O}\). However, when looking the energy balance before and after such collisions (either strongly endothermic or strongly exothermic) it becomes clear that under the present physical conditions both processes can be neglected.
3.3 Rate equations

To get the theoretical relationships between the relevant number densities, a proper set of rate equations have to be defined. As mentioned before, the plasma jet burns in a quasi-stationary regime. Therefore, the steady-state rate equations for relevant number densities appearing in the above reactions can be applied. The collision rates $R$, introduced above, are usually defined as products of corresponding rate coefficients $k$ (units: s$^{-1}$ cm$^3$) and the collision partner number density $n$ (cm$^{-3}$). In general, each of the described collisional excitation energy processes between particular initial $i$ and final state $f$ (characterized by rate coefficient $k_{i,f}$) is followed by the reverse reaction (rate coefficient: $k_{f,i}$). The principle of the detailed balancing predicts, that 

$$ \frac{k_{i,f}}{k_{f,i}} \propto \exp(-\Delta E_{f,i}/kT) $$

where $\Delta E_{f,i}$ is the energy difference between the final and the initial state. Under the present experimental conditions, with proper estimates for the excited state number densities, the processes reverse to the collisional excitation energy transfers listed above can be neglected. This approximation leads to a simple set of linear steady-state rate equations related to the number densities $n_0$, $n_1$ and $n_2$ of He, He$^+$, He$, respectively, as well as to the relevant number densities of nitrogen ($n_3^i$, $n_4^i$, $n_5^i$) and water ($n_1^{	ext{III}}$):

$$ \frac{dn_2}{dt} = 0 = R_P n_0 - A_{21} n_2 $$

$$ \frac{dn_1}{dt} = 0 = A_{21} n_2 - (R_A + R_D) n_1 $$

$$ \frac{dn_4^i}{dt} = 0 = R_A n_1 - A_{43} n_4^i $$

$$ \frac{dn_3^i}{dt} = 0 = A_{43} n_4^i - (R_B + \sum_{j=0}^2 R_{3j}^i) n_3^i $$

$$ \frac{dn_1^{	ext{III}}}{dt} = 0 = R_B n_3^i - (R_C + R_S + R_P^i) n_1^{	ext{III}} $$

$$ \frac{dn_2^i}{dt} = 0 = R_C n_1^{	ext{III}} + R_{32}^i n_3^i - (A_{21} + A_{20}^i) n_2^i $$

The collisional pump rate $R_P$ for the electron impact excitation process (3.5) is defined as the product of the corresponding rate coefficient $k_P$ and the number density $n_{el}$ (cm$^{-3}$) of electrons. In the present weakly ionized plasma,
helium ground state number density $n_0$ equals to total helium atom number density $n_{He}$. Thus, the positive contribution in Eq. (3.16) can be written as $R_p n_0 = k_p n_{el} n_{He}$. The electron-induced de-excitation rate for the metastable state is defined as: $R_D = k_D n_{el}$, while the rate is $R_A = k_A n_0 = k_A n_{N_2}$. Here, for the same reason as in case of He, the ground state number density $n_0$ is replaced with total density $n_{N_2}$. Furthermore, we have $R_B = k_B n_0 = k_B n_{H,O}$, $R_{3j}^{el} = k_{3j}^{el} n_{el}$ and $R_{S}^{el} = k_{S}^{el} n_{el}$. The rate $R_p^{el}$ in Eq. (3.20) symbolizes the sum of all rates related to additional depopulation processes (3.15). Depending on the kind of collision partners $M_1$ (either electrons or air components) these rates can be either in the form $R_p^{el}(e^-) = k_p^{el} n_{el}$ or $R_p^{el}(comp) = k_p^{comp} n_{comp}$.

The investigated plasma jet is strongly inhomogeneous. It is obvious that the solutions to the set of rate equations (3.16 - 3.21) exhibit complex dependences on position in the jet. Nevertheless, well-defined and very different $x$-dependences of helium and air components become a helpful tool in further analysis.

3.4 Modeling of line intensity distributions

We consider the He, N$_2^+$, and N$_2$ lines emitted at frequencies $\nu_{21}, \nu_{43}^l$, and $\nu_{21}^l$. In the optically thin case, their intensities are $I_{He}(\nu_{21}) \propto A_{21} n_2$, $I_{N_2}(\nu_{43}^l) \propto A_{43}^l n_4^l$, and $I_{N_2}(\nu_{21}^l) \propto A_{21}^l n_2^l$, respectively.

He lines:
Rate equation (3.16) with the substitution $R_p = k_p n_{el}$ yields following simple spatial dependence of helium line intensities along the x-axis:

$$I_{He}(\nu_{21}, x) \propto n_{el}(x) n_{He}(x) \quad (3.22)$$

Then, with exponential decrease of electron and helium density adopted above, the expected position-dependent intensities of He optically thin lines are of the following simple form:
\[ I_{He}(v_{21}, x) \propto \exp[-(a+b)x], \quad (3.23) \]

**N\textsubscript{2}\textsuperscript{+} lines:**

Combination of Eqs. (3.17) and (3.18) and expression (3.22) yields the following relation between the position-dependent intensities of N\textsubscript{2}\textsuperscript{+} and He lines

\[ I_{N_2}(v_{43}, x) \propto \Psi(x) I_{He}(v_{21}, x), \quad (3.24) \]

where the function \( \Psi(x) \) is given by

\[ \Psi(x) = \frac{R_A(x)}{R_A(x) + R_D(x)} \quad (3.25) \]

As one can see from Figs. 2 and 3, spatial distributions of N\textsubscript{2}\textsuperscript{+} lines strongly differ from the distributions of He lines. This means that the function \( \Psi(x) \) has a pronounced dependence on \( x \). Up to our knowledge, the values for collisional rate coefficients needed for calculation of distribution (3.24), cannot be found in the literature. In addition, in the framework of the present investigation the electron number density has not been measured. However, one can circumvent the lack of these data and search for conditions at which the function \( \Psi(x) \) exhibits the most pronounced \( x \)-dependence. For this purpose, the ratio \( \frac{R_A(x)}{R_D(x)} = k_A n_{N_2}(x)/k_D n_e(x) \) is crucial and we consider two extreme cases regarding this parameter.

**Case 1:** \( R_A(x) \gg R_D(x) \)

In this case the function \( \Psi(x) \) equals nearly to 1, which means that, according to expression (3.24), the \( I_{N_2}(v_{43}, x) \) should acquire the exact shape of He lines distribution. This is strongly opposite with the present experimental findings, and therefore the case 1 can be excluded.

**Case 2:** \( R_A(x) \ll R_D(x) \)

In this case the term \( k_A n_{N_2}(x) \) in the denominator of expression (3.25) can be neglected, and \( \Psi(x) \approx \frac{R_A(x)}{R_D(x)} \), which corresponds to the case when
\( \Psi(x) \) acquires a most pronounced dependence on position \( x \). According to expressions (3.22), (3.24) and (3.25), the shape of \( N_2^+ \) line intensity distributions becomes

\[
I_{N_2^+}(v'_{43}, x) \propto n_{N_2}(x) n_{He}(x) \quad R_d(x) \ll R_D(x) \quad (3.26)
\]

Thus, with previously defined normalized spatial density distributions for helium (see Eq. (3.1)) and nitrogen molecules (Eq. (3.3)), the approximate relation (3.26) becomes:

\[
I_{N_2^+}(v'_{43}, x) \propto \left[1 - \exp(-a x) \right] \exp(-a x) \cdot R_d(x) \ll R_D(x) \quad (3.27)
\]

**\( N_2 \) lines:**

By combining Eqs. (3.18-3.21) one obtains the following relationship between the neutral and ionized nitrogen intensity line distributions: \( I_{N_2}(v'_{21}, x) \) and \( I_{N_2^+}(v'_{43}, x) \):

\[
I_{N_2}(v'_{21}, x) \propto \Phi(x) I_{N_2^+}(v'_{43}, x) \quad (3.28)
\]

where function \( \Phi(x) \) reads:

\[
\Phi(x) \propto \frac{R_B(x)}{R_B(x) + \sum_{j=0}^{2} R_{ij}(x)} \left[ \frac{R_{2c}(x)}{R_B(x) + R_c(x) + R_s^\parallel(x) + R_p^\parallel(x)} \right] \quad (3.29)
\]

As shown in Section 2, in the investigated plasma jet these distributions are very different too. In order to determine the conditions which yield most pronounced x-dependence of \( \Phi(x) \), we examine extreme cases in the same straightforward manner as previously. These extreme cases are defined by relationships between the rate \( R_B(x) \) and the sum of recombination rates

\[
S(x) = \sum_{j=0}^{2} R_{ij}(x) \quad \text{as well as between} \quad R_c \quad \text{and} \quad R_s^\parallel + R_p^\parallel. \quad \text{For the sake of clarity, four possible extreme combinations and corresponding approximate forms of} \quad \Phi(x) \quad \text{are listed in Table 1.} \]
Table 1. Approximate expressions for the function $\Phi(x)$

<table>
<thead>
<tr>
<th>Case</th>
<th>Expression</th>
<th>Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3: $R_B(x) \ll S(x)$, $R_C \ll (R_S^| + R_P^|)$</td>
<td>$\Phi(x) \propto R_{S2}^| (x) / S(x) = k_{S2}^| / \sum_{j=0}^{2} k_{3j}^|$</td>
<td></td>
</tr>
<tr>
<td>4: $R_B(x) \ll S(x)$, $R_C \gg (R_S^| + R_P^|)$</td>
<td>$\Phi(x) \propto (k_{S2}^| / \sum_{j=0}^{2} k_{3j}^|) + 1$</td>
<td></td>
</tr>
<tr>
<td>5: $R_B(x) \gg S(x)$, $R_C \gg (R_S^| + R_P^|)$</td>
<td>$\Phi(x) \propto 1$</td>
<td></td>
</tr>
<tr>
<td>6: $R_B(x) \gg S(x)$, $R_C \ll (R_S^| + R_P^|)$</td>
<td>$\Phi(x) \propto \frac{k_c n_{N_2}(x)}{(k_S^| + k_p^{el}) n_{el}(x) + k_p^{comp} n_{comp}(x)}$</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen in Table 1, only in the case 6 the function $\Phi(x)$ acquires a form which strongly depends on position $x$. In all other cases $\Phi(x)$ becomes constant, which would imply equal distributions of nitrogen ion and neutral lines. Therefore, we continue our consideration for the case 6). It should be stressed that, compared with other possibilities when the relevant rate ratios acquire constant values, the case 6) yields the most pronounced functional dependence $\Phi(x)$. However, when looking at the denominator of the approximate expression for $\Phi(x)$ in the case 6), once again we have two extreme possibilities at disposal. First, if $(k_S^\| + k_p^{el}) n_{el}(x) \ll k_p^{comp} n_{comp}(x)$, $\Phi(x)$ would be independent of position and consequently, the spatial distributions of $N_2$ lines would not differ from the $N_2^+$ line distributions. Therefore, this case (called 6a) can be excluded and we continue our consideration for the case 6b) where $(k_S^\| + k_p^{el}) n_{el}(x) \gg k_p^{comp} n_{comp}(x)$.

In this case, with adopted distributions $n_{H_{2}0} \propto [1 - \exp(-ax)]$ and $n_{el}(x) = \exp(-bx)$, the spatial distributions of neutral nitrogen molecule lines are of the following shape.

$$I_{N_2}(v_{21}, x) \propto [1 - \exp(-ax)]^2 \exp[-(a+b)x] \quad \text{(cases 2 and 6b)} \quad (3.30)$$

Referring to case 6b an introduction of organic molecules should be performed at the position where the maximum of $N_2^+$ is located in order to get...
an efficient protonation. A change of the N\textsubscript{2} concentration should be the consequence.

3.5. Comparison of the experiment and modeling
As representatives of He, N\textsubscript{2}\textsuperscript{+}, and N\textsubscript{2} optically thin lines, the data for the lines at 706 nm, 427 nm and 380 nm, respectively, are plotted in Figs. 6 and 7. The intensities were measured in arbitrary units along the x-axis for lower (F\textsubscript{A}) and higher (F\textsubscript{B}) helium flow through the capillary. Intensities presented in Fig 6 and 7 are extracted (z = 0) from the data presented in Figs. 2 and 3, respectively.

![Fig. 6. Comparison of experimental (symbols) and modeled (lines) intensity distributions for the He 706 nm (left), N\textsubscript{2}\textsuperscript{+} 427 nm and N\textsubscript{2} 380 nm lines (right) at lower helium flow F\textsubscript{A}. The experimental error bars are of the size of the symbols. See further explanations in the text.](image)
Fig. 7. Comparison of experimental (symbols) and modeled (lines) intensity distributions for the He 706 nm (left), $N_2^+ 427$ nm and $N_2 380$ nm lines (right) at higher He flow $F_B$. The experimental error bars are of the size of the symbols. See further explanations in the text.

The experimental distributions are plotted together with fitted theoretical distributions. Following the previous considerations and notation, the $x$-dependent intensity distributions for the He 706 nm, $N_2^+ 427$ nm, and $N_2 380$ nm line intensities can be described by:

\[ I(706) = C_{706} \exp[-(a+b)x] \]  

\[ I(427) = C_{427} [1 - \exp(-a \cdot x)] \exp(-a \cdot x) \qquad \text{(case 2)} \]  

\[ I(380) = C_{380} [1 - \exp(-a \cdot x)]^2 \exp[-(a-b) \cdot x] \qquad \text{(cases 2 and 6b)} \]

The values of scaling factors $C_{\lambda}$ are expressed in arbitrary units. The data for the He 706 nm line are presented in semi-logarithmic plots together with the corresponding fitting functions. With the exception of the data obtained at the flow $F_B$ for the $x$-values closest to the capillary orifice, there is a good agreement with the predicted exponential behavior of the helium lines. The deviations of the first two points from the exponential decrease can be explained by optical thickness of the He 706 nm line in this region at higher flow rate. By comparing analogous distributions of various He lines, it
becomes evident that such deviations close to the capillary orifice are correlated with their increased optical thickness indeed. The fitted values \((a + b)\) for the lower \(F_A\) and the higher flow \(F_B\) are 0.8 cm\(^{-1}\) and 0.33 cm\(^{-1}\), respectively, with statistical errors less than 5%. Here, in the case of \(F_B\), the first two points were not included in the fitting procedure.

As shown in Section 2, the distributions for various \(N_2^+\) lines are, within the error bars, mutually of the same shape. Therefore, one can conclude that these lines are optically thin in the whole examined jet region and their intensity distributions can be directly connected with \(n_{i_2}'\). Analogous conclusion is valid for \(N_2\) lines and their connection with \(n_{i_2}'\). In Figs. 6 (right) and 7 (right) the approximate expressions (3.32) and (3.33) are fitted to the \(N_2^+\) 427 nm (full gray lines) and the \(N_2\) 380 nm (full black lines) intensity distributions. The parameters \(a\) and \(b\) for a given helium flow rate are determined by measured value \((a+b)\) and experimental positions of intensity distribution maxima. Since Eqs. (3.32) and (3.33) are coupled, the simulations for both 427 nm and 380 nm at the given He flow rate should be described by the same value of the parameter \(a\). However, this matching cannot be exactly achieved, and the best fitting for both distributions can be obtained for \(a_A = (0.55 \pm 0.05)\) cm\(^{-1}\) at lower and \(a_B = (0.25 \pm 0.03)\) cm\(^{-1}\) at the higher helium flow rate, combined with the corresponding values for \(b_A = (0.80 - a_A)\) and \(b_B = (0.33 - a_B)\). The factors \(C_i\) were obtained by fitting to the values of experimental distributions maxima.

As one can see from Figs. 6 and 7, the experimental intensity distributions of the \(N_2^+\) 427 nm line are narrower than the theoretical ones. As for the condition given by case 1 \((R_A(x) \ll R_D(x))\), a more detailed numerical analysis shows that the calculated distribution (3.32) slightly changes if the ratio \(R_A(x) / R_D(x)\) acquires the values between 0 and 0.5. On the other hand, the \(N_2\)-line distributions are well described by functional shape given by Eq. (3.33). It should be noted that according to the condition 6b, only a small portion of \((H_2O)^+\) is depopulated due to collisions with \(N_2\), which is governed by the small rate \(R_C(x) \ll R_5'' + R_P''\). The appearance of highly excited \(N_2\) molecules serves in the present case as a detector of generated ionized water.
and indicates the position in the plasma jet where the further reactions involving \((\text{H}_2\text{O})^+\) could occur.

A general agreement between measurement and modeling confirm two facts. First, both theoretical and experimental distributions are broader at higher helium flow rate, and second, both simulated curves at higher flow rate are shifted towards larger distances from the capillary orifice.

4. Discussion and conclusions

The performed spatially resolved spectroscopic measurements on a dielectric barrier discharge plasma jet confirmed results of previous investigations and yielded additional insight into the relevant excitation energy processes leading to the pronounced ionization of water in the air and the subsequent protonation of organic molecules for soft ionization.

A map of the intensities distribution in the plasma jet of some relevant emission lines of the species involved in the energy transfer process (\(\text{He} 706\) nm, \(\text{N}_2 380\) nm and \(\text{N}_2^+ 427\) nm) for two different gas flows \((300\) and \(1000\) ml min\(^{-1}\)) has been presented. The plasma jet, which penetrates from the zone of the capillary barrier discharge into the atmosphere has strongly non-homogeneous distribution of the ground-state particles. However, the jet is axially symmetric and its non-homogeneity along the axis of penetration is well defined. This constituted an important starting point in the presented modeling.

A simplified semi-quantitative theoretical model that describes the energy transfer processes involving \(\text{He}, \text{N}_2\) and \(\text{H}_2\text{O}\) in their ground, excited and ionized states is presented. Using this model and taking the experimental parameters into account, the number density distributions of excited \(\text{He}, \text{N}_2^+\) and \(\text{N}_2\) along the plasma jet were simulated and compared with the intensity distributions of the corresponding optically thin spectral lines observed in the experiment.

It is not to expect that the presented approximate expressions for the number density distributions, i.e. intensity distributions show an excellent agreement
with the complex situation in the investigated plasma jet. However, there is a general agreement with the experiment, which is confirmed by the reproduced position of the line intensity maxima as well as their shifting towards larger distances from capillary orifice. In turn, one can conclude that the main excitation path leading to ionization of water is described by relationships between relevant rates as defined in Section 3. In addition, a region in the plasma jet characterized by the most efficient subsequent protonation of sample molecules was identified and will be the subject of further investigations.

Acknowledgement

Financial supports by the Deutsche Forschungsgemeinschaft, the Ministry of Innovation, Science, Research and Technology of the state North Rhine Westphalia, the Ministry of Education and Research of the Federal Republic of Germany, the Ministry of Science, Education and Sports of the Republic of Croatia (project No. 035-0352851-2853) are gratefully acknowledged.

References


