Mechanism of N\textsubscript{2} dissociation and kinetics of N(\textsuperscript{4}S) atoms in pure nitrogen plasma

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Abstract. This work deals with kinetics of the ground state nitrogen atoms N(\textsuperscript{4}S) and N\textsubscript{2} dissociation mechanism in pure nitrogen plasma. The experiment was carried out in positive column of DC glow discharge at a range of parameters p = 5 – 50 Torr, J = 20 – 100 mA. The use of axial homogeneous glow discharge allowed considering N(\textsuperscript{4}S) balance for spatially uniform conditions controlled by only two terms: source (characterized by effective production rate \(k_{\text{diss}}^\text{eff}\)) and loss (characterized by effective loss time \(\tau_{\text{loss}}^N\)). Analysis of these parameters gains considerably better understanding of N\textsubscript{2} dissociation mechanism in pure nitrogen plasma that was the main goal of the given work. So N/N\textsubscript{2} dissociation rate as function of discharge parameters was obtained using two independent emission optical methods: actinometry on Ar atoms and N\textsubscript{2}\textsuperscript{2+} band emission decay at discharge modulation. Measurements of N/N\textsubscript{2} radial profiles allowed estimating N atom surface loss probability \(\gamma_{\text{loss}}^N\) and correspondingly \(\tau_{\text{loss}}^N\). It was revealed that \(\gamma_{\text{loss}}^N\) depends on N(\textsuperscript{4}S) concentration and thereby discharge conditions through the sorption balance of physisorbed N atoms. Simple phenomenological model taking into account basic surface processes provides \(\gamma_{\text{loss}}^N\) data in good agreement with experiment. Finally, \(k_{\text{diss}}^\text{eff}\) was obtained as function of reduced electric field E/N and it was shown that even EEDF self-consistently calculated with accounting for N\textsubscript{2} vibrational excitation is unable to provide observed values of \(k_{\text{diss}}^\text{eff}\). Reasons of that fact are discussed in detail.

1. Introduction
At the increased pressure the associative ionization is the main ionization mechanism in nitrogen plasma [1]. Crucial point is that nitrogen molecules are able to accumulate considerable energy in their vibrations because of (v-v) exchange processes. Through the intermediate agents this energy is spent on excitation of electronic states of atoms and molecules which consequentially participate in associative ionization processes. Despite of big interest to nitrogen plasma, mechanism of such energy transmission has not been studied yet in details. Metastable \(N_2(A^3\Sigma_u^+)\) molecules and \(N(\text{^2}P)\) atoms are believed to be most probable intermediate agents [1] that realize energy stored in N\textsubscript{2} vibrations into N\textsubscript{2} ionization. Since direct N\textsubscript{2}\textsuperscript{+} production in collision of two \(N_2(A^3\Sigma_u^+)\) molecules is impossible, the mechanism of associative ionization has to include few steps with using other particles. Such particles...
can be nitrogen atoms. So, as a first step, it was studied N(4S) kinetics in pure N2 plasma of positive column (PC) of DC - glow discharge at pressures 5 - 40 Torr. Such type of plasma is sufficiently suitable test object for this research because it is longitudinally homogeneous and radially symmetrical. Besides, this type of discharge is relatively easy to sustain.

Here N(4S) balance in plasma was considered in simple zero-dimensional form, controlled by only two terms: source and drain:

\[ \frac{dN(4S)}{dt} = k_{\text{eff}} n_e N_2(X^1\Sigma_g^+, v) - \frac{N(4S)}{\tau_{\text{loss}}} \]  

(1.1)

where \( N(4S) \), \( N_2(X^1\Sigma_g^+, v) \) are concentrations of ground state N atoms and ground state vibrationally excited N2 molecules respectively, \( n_e \) – electron concentration. Source term comprises all possible ways of \( N(4S) \) production (i.e. N2 dissociation reactions of all possible electronic and vibrational states) and characterized by effective production rate – \( k_{\text{eff}} \). Similarly, depletion term includes all mechanisms of atoms’ loss and characterized by effective depletion time \( \tau_{\text{loss}} \).

Since in equilibrium conditions:

\[ \frac{dN(4S)}{dt} = 0 \]  

(1.2)

So, according to (1.1) \( k_{\text{eff}} \) and \( \tau_{\text{loss}} \) reveal to be related.

Thus, goal of this work is to examine kinetics of \( N(4S) \) in pure nitrogen plasma. This comprises determination of \( N(4S) / N_2 \) dissociation rate versus discharge parameters – electric field and pressure – over whole operating range. Secondly, experimental obtaining of \( \tau_{\text{loss}} \) based on analysis of loss processes. Finally, using above mentioned relation with \( \tau_{\text{loss}} \), one can evaluate \( k_{\text{eff}} \) as well as establish it’s dependence on discharge parameters. Further analysis of obtained \( k_{\text{eff}} \) values and comparison with theory afford considerably better understanding of N2 dissociation processes in pure nitrogen plasma.

2. Experiment

2.1. Setup

Experimental setup is shown on figure 1. Discharge operated in cylindrical quartz tube with MgF2 windows. Tube’s wall was cooled by flowing water. Electric current, applied voltage and optical signal were acquired using NI Data Acquisition (DAQ) board (1) and further transferred to PC (2). Optical emission from the tube’s interior was collected by objective (3) and directed on the entrance slit of the monochromator (4). Distance from the tube’s center to the monochromator varied from several cm to 2m approximately. Commonly tube was adjacent to monochromator when optical measurements in the tube’s axis region were needed. Such measurements were accomplished with photomultiplier tube (PMT) (5). Large distance was chosen for optical measurements on the tube’s cross-section with high spatial resolution. In this case (Intensified Charge Coupled Device) ICCD matrix (6) was used.
2.2. Gas temperature determination with emission optical method

Knowledge of gas temperature for every used discharge regime is necessary in this work. Spectrum of light emitted by plasma is sensitive to ohmic gas heating. Therefore spectrum’s shape could contain information about $T_{\text{gas}}$. Indeed, the spectrum is defined by structure of $N_2$ electronic – vibrational – rotational levels and by distribution of molecular population of these levels (see, for example, [2]).

Here we used several bands of second positive system $N_2(C'\Pi_g, v'–B'\Pi_g, v")$. Molecular population of rotational levels of upper states obeys Boltzmann distribution which is characterized by rotational temperature $T_{\text{rot}}$. Because of intensive collisional exchange between energies of rotational and translational motions $T_{\text{rot}}$ reveals to be related to $T_{\text{gas}}$ and very close to it by magnitude.

Thus, it was created computer model of $N_2$ emission spectrum where $T_{\text{gas}}$ was the main parameter. Comparing model spectrum with experimental one it was determined $T_{\text{gas}}$ in the tube’s axis region as function of discharge parameters (figure 2).

Emission spectrums of the same spectral range but obtained with lesser resolution was used for spatial determination of $T_{\text{gas}}$ or getting it’s dynamics in time. In that method [3] was used the fact that ratio of maximal intensities of P – and R – branches defines spectrum’s shape and consequently $T_{\text{gas}}$. With mentioned above computer model of emission spectrum it was determined a calibration curve ($T_{\text{gas}}$ versus the ratio). It is worth noting that shape of the curve strongly depends on a monochromator’s apparatus function.

Therefore in experiments only the ratio of the intensities was determined over whole tube’s cross section. Next, the obtained radial profile of the ratio was recalculated to $T_{\text{gas}}$ radial profile (using the calibration curve). Evaluated in that way $T_{\text{gas}}$ radial profiles revealed to be nearly homogenous almost up to tube’s wall for all used regimes of discharge. In other words, gas temperature in the tube was accepted to be approximately constant having value of that in the tube’s axis region.

2.3. Reduced field $E/N$

Reduced field $E/N$ (here $E$ – electric field, $N$ – concentration of neutrals) is a crucial parameter of any type plasma (which define electron energy distribution function (EEDF), reaction rates, etc). That is why this research requires specific values of $E/N$. Electric field in positive column was evaluated as $E=(V–V_{\text{cpd}})/L$ where $V$ – applied voltage, $V_{\text{cpd}}$ – cathode potential drop (values were taken from literature), $L$ – length of the positive column (11 cm). Concentration of neutrals was calculated according to $P=Nk_{\text{Bol}}T_{\text{gas}}$ (here $P$, $T_{\text{gas}}$ – gas pressure and temperature correspondingly, $k_{\text{Bol}}$ – Boltzmann constant). Using $T_{\text{gas}}$ data obtained previously, $E/N$ was evaluated as function of discharge parameters (figure 3). Radial profile of the reduced field $E/N$ in the tube was accepted to be uniform due to $T_{\text{gas}}$ radial uniformity (mentioned in section 2.2).
2.4. \(N(4S)\) concentration and \(N/N_2\) dissociation rate experimental obtaining

Absolute concentrations of \(N(^4S)\) (as well as \(N/N_2\) dissociation rate) on the tube’s axis were determined using two independent techniques.

The first technique is actinometry with Ar atoms (5% Ar and 95% \(N_2\)). That was implemented in a similar manner with [4] where detailed description of the method was made. Obtained in that way results (figure 4) are highly dependent of corresponding actinometrical constants and, eventually, of calculated EEDF. (For \(N_2\) plasma of used pressures the most essential way to obtain EEDF is to calculate it numerically using programs such as BOLSIG+). Thus inaccuracy of \(N/N_2\) estimation with actinometry is defined mostly by the calculated EEDF.

These considerations gave motivation to perform this experiment once again in other way – using \(N_2(C^3Π_u)\) radiation dynamics under electric current modulation. This method [5] was originally applied in studies of afterglows and has an advantage to be EEDF insensitive.

Obtained with two methods \(N/N_2\) values are in good agreement (figure 5). However \(N/N_2\) dependencies on discharge parameters (pressure, current) are somewhat different. Further analysis of that fact is needed. Comparison of the results allows us to test EEDF calculation adequacy as well as accuracy of commonly used actinometric constants.

\[\text{Figure 4. Obtained using actinometry method dissociation rate } N/N_2 \text{ as function of discharge parameters (for the tube’s axis region).}\]

\[\text{Figure 5. Absolute concentrations } N(^4S) \text{ (for the tube’s axis region) determined with actinometry (solid symbols) and using “modulation technique” (crossed symbols).}\]

2.5. \(N\) atom surface loss probability \(\gamma_{\text{loss}}^N\)

Simple estimations showed that for used pressures (\(p = 5 – 50\) Torr) main \(N\) atom loss mechanism is recombination on tube’s wall which proceeds according to \(N + N \rightarrow N_2\). Quantitatively the probability of this process is characterized by value of \(\gamma_{\text{loss}}^N\). This quantity is essentially related with mentioned in introduction \(\tau_{\text{loss}}^N\) (\(N\) atom effective loss time):

\[
\tau_{\text{loss}}^N \equiv \frac{2R}{v_T^N} \gamma_{\text{loss}}^N
\]

(2.5.1)

where \(v_T^N = \sqrt{\frac{8kT}{\pi M_N}}\) - average thermal speed of \(N\) atoms, \(R\) – tube’s radius

Obviously, the first factor represents atom’s diameter passage time. According to literature \(\gamma_{\text{loss}}^N\) has order about 0.01 – 0.001 what means that effectively atom passes the tube’s diameter 100 – 1000 times before recombination. \(\gamma_{\text{loss}}^N\) was evaluated as function of discharge parameters using \(N(^4S)/N_2\) radial profiles (analogically with [6]). It was revealed that \(\gamma_{\text{loss}}^N\) depends on \(N(^4S)\) concentration and thereby discharge conditions through the sorption balance of physisorbed \(N\) atoms (figure 6).
To achieve better understanding, basic surface processes were considered in much the same way with work [6]. As a result simple phenomenological model was created. The model provides $\gamma_{\text{loss}}$ (as function of discharge parameters) in good agreement with experiment indicating satisfactory level of understanding (figure 7).

3. Effective N($^4\text{S}$) production rate $k_{\text{eff}}^{\text{diss}}$ and discussion.

According to equation (1.1) taking into account equilibrium condition (1.2) the effective N($^4\text{S}$) production rate $k_{\text{eff}}^{\text{diss}}$ could be expressed as:

$$k_{\text{eff}}^{\text{diss}} = \frac{\gamma_{\text{loss}}^{\text{N}} V_{\text{eff}}^N}{n_e} \cdot \frac{N(4S)}{N_2}$$  \hspace{1cm} (3.1)

$n_e$ – electron concentration (evaluated from electric current $J = e n_e v_{\text{diss}}^e$), other quantities were mentioned above. Using above obtained data $k_{\text{eff}}^{\text{diss}}$ was evaluated versus reduced field $E/N$ and showed on figure 8 with symbols. Solid line represents theoretical rate dissociation constant in electronic collisions with vibrationally unexcited $N_2$ molecules of the ground state. It can be seen that nitrogen dissociation in $N_2$ plasma proceeds with higher rate than it is predicted by theory with the difference being notable (few orders) at low $E/N$.

$k_{\text{eff}}^{\text{diss}}$ is highly sensitive to EEDF. For $N_2$ plasma of mentioned pressures the most essential way to obtain EEDF is to calculate it using programs such as BOLSIG+. EEDF used for theoretical $k_{\text{eff}}^{\text{diss}}$ was calculated without consideration of $N_2$ vibrational excitation. However, transformation of EEDF due to $N_2$ vibrational excitation does not allow explaining solely the difference between theory and experiment. $k_{\text{eff}}^{\text{diss}}$ calculated with such EEDF reveals to be still some orders of magnitude lesser than the experimental one. It means that particles having low energy threshold to $N_2$ dissociation fully
controls N(4S) production. N2(v) molecules on Treanor plateau are the most probable candidates for it. Rough estimation of effective energy threshold of N2 dissociation in plasma gives value 2 – 3 eV, which corresponds to Treanor plateau in energy scale. It is also known, that intensive energy exchange exists between vibrationally excited molecules N2(v) of Treanor plateau and N2 (A3Σ_u^+) molecules. Role and significance of N2 (A3Σ_u^+) in N2 dissociation haven’t been completely understood yet. Detailed mechanism of N2 dissociation in nitrogen plasma still has been needed in the following research.

Figure 8. k_{eff} experimental (symbols) and theoretical (solid line).

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