

# Nitrogen dissociation in low-pressure microwave plasmas

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## Abstract.

This work reviews a number of important aspects of the kinetic processes occurring in microwave discharge plasmas in nitrogen containing mixtures. The fundamental problems which are addressed include: (1) the determination of the non-equilibrium electron energy distribution function and its coupling to the vibrational kinetics; (2) the processes determining the vibrational distribution function in  $N_2$ ,  $N_2$ - $H_2$ , and  $N_2$ -Ar plasmas; and (3) the influence of surface kinetic processes on the whole discharge physics. The mechanisms of dissociation and ionization in  $N_2$ ,  $N_2$ -Ar and  $N_2$ - $H_2$  are discussed in detail. The important role of plasma-wall interactions is stressed. It is shown that in  $N_2$ -Ar mixtures there is an increase in the dissociation degree of  $N_2$  molecules at high Ar fractional concentrations, which can be ascribed to the contribution of fast  $Ar^+ + N_2 \rightarrow N_2^+ + Ar$  exchanges followed by  $N_2^+$  dissociative recombination. It is further demonstrated that surface electron-ion recombination processes involving  $NH_2^+$  and  $N_2^+$  ions are the most important sources of  $N(^4S)$  gas phase atoms in  $N_2$ - $H_2$  mixtures. As the amount of  $H_2$  in the discharge increases, the channel associated with  $HN_2^+$  ions becomes dominant. At nearly constant electron density there is a smooth decrease in the dissociation degree of hydrogen in  $N_2$ - $H_2$  when the  $H_2$  percentage increases up to 50%, which is due both to electron impact dissociation and  $H_2$  dissociation upon quenching of nitrogen  $N_2(A^3\Sigma_u^+)$  and  $N_2(a'^1\Sigma_u^-)$  metastables.

## 1. Introduction

Microwave discharges in pure nitrogen and nitrogen containing mixtures keep attracting scientists and researchers nowadays, due to their interest both to applications and to fundamental research. As a matter of fact, these discharges produce a very rich plasma, whose complexity arises from the interplay between different kinetics, namely electron, vibrational, chemical and surface kinetics. The elementary processes ruling the discharge behavior are thus strongly non-linear and require a careful investigation. Microwave low-pressure discharges driven by the field of a surface wave constitute a very interesting source to the study of these plasmas, since they have a wide range of operation and are accessible to a variety of experimental diagnostics. Furthermore, they provide high number densities of the active species of importance for the technological applications, such as ground state atoms and atomic and molecular excited metastable states,

In this work we restrict our investigation to surface wave discharges produced in the most common geometry, consisting of a discharge in a long cylindrical column with a radius of the order of the cm. The source is operated either at a frequency  $\omega/2\pi = 2.45$  GHz or 500 MHz,

at low-pressure conditions,  $p = 0.5$  Torr, in  $N_2$ ,  $N_2$ -Ar and  $N_2$ - $H_2$ . Self-consistent theoretical models for these systems have been developed in the last years, so that only a few notes on how to build these models and to describe the coupling between the different kinetics are given in this paper. The reader should refer to [1]–[5] for details and literature survey on  $N_2$ , to [5]–[8] for  $N_2$ -Ar, and to [5, 9, 10] for  $N_2$ - $H_2$ . Nevertheless, it is worth noting that the input parameters of the model are the ones usually controlled externally in a real experiment, namely gas pressure, wave frequency, tube radius, and electron density at the position of the launcher (which is controlled through the power delivered to the launcher). The model is based on a set of coupled equations for the plasma bulk describing kinetics of free electrons, the vibrational kinetics of molecules in the electronic ground states, the kinetics of excited atoms and molecules, the chemical kinetics of neutrals and ions, the gas thermal balance, and the charged particle balance determining the electric field sustaining the discharge. A set of equations for the wave dispersion properties and power balance is included in order to close the formulation.

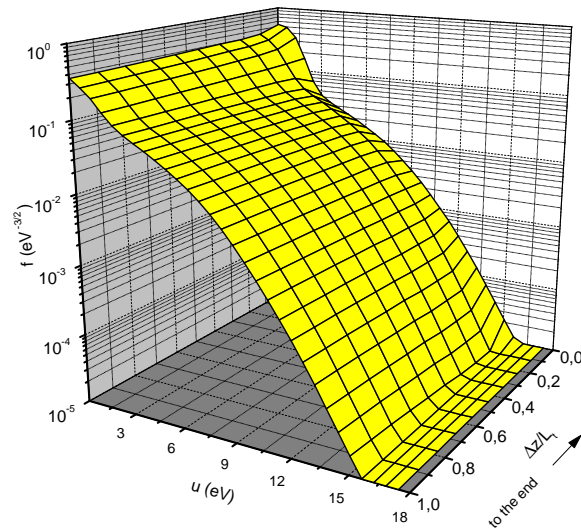
It is not possible to address in a short paper the kinetic process in molecular gases in general. We have decided to illustrate that self-consistent modeling is a powerful tool to investigate these processes, by structuring this paper as follows. Some results about the electron kinetics and its coupling to the vibrational kinetics are discussed first. The dissociation processes in  $N_2$ ,  $N_2$ -Ar and  $N_2$ - $H_2$  are subsequently analysed in some detail. The last section summarizes the main results pointing out the important role of plasma-wall interactions.

## 2. Electron and vibrational kinetics

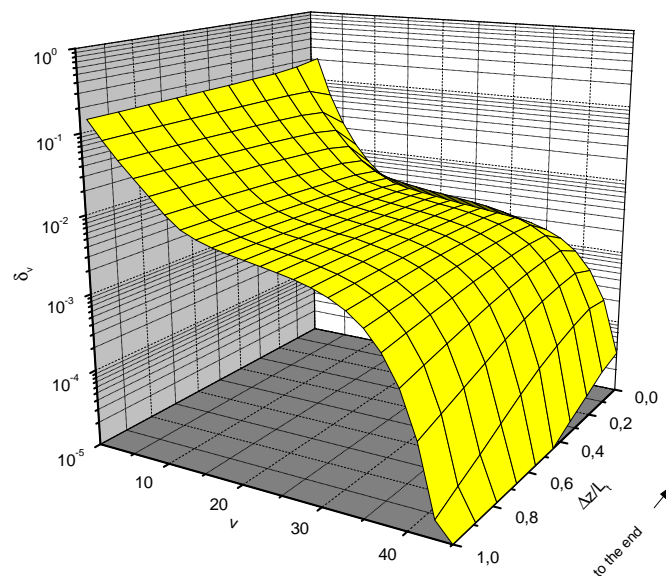
In gas discharges electrons gain energy from the electric field and redistribute it through collisions among the atomic and molecular internal degrees of freedom, dissociation and ionization. These processes of electron energy gain and loss are adequately described by the quasi-stationary electron Boltzmann equation, which allows the calculation of the electron energy distribution function (EEDF). In the references cited above, the anisotropies caused by spatial inhomogeneities and the field are assumed to be sufficiently small, and the electron velocity distribution is approximated by the usual two-term expansion in spherical harmonics. Electron collisions of the first and the second kind and electron-electron collisions are accounted for. Since vibrationally excited molecules in nitrogen containing discharges constitute an appreciable fraction of the total molecular population, the EEDF is generally a functional of the vibrational distribution function (VDF) of ground state molecules of  $N_2$  and of the other molecular species present in the plasma ( $H_2$  in the present case). Under steady-state conditions the power absorbed from the surface-wave field per electron is equal to the net power lost per electron due to all kinds of electron collisions, and an electron power balance equation can easily be written[1].

The VDFs of ground-state molecules  $N_2(X^1\Sigma_g^+, v)$  and  $H_2(X^1\Sigma_g^+, v)$  (if present) are strongly coupled to the electron kinetics, due to inelastic and superelastic electron collisions (e-V processes). The other processes determining the population of molecules in vibrationally excited levels are vibration-vibration (V-V) and vibration-translation (V-T) energy exchanges, deactivation of vibrationally excited molecules at the wall, dissociation from vibrationally excited levels, atomic recombination, and heavy-particle reactions involving vibrationally excited molecules. The later processes include the usual mechanisms of population of the vibrational levels in collisions involving electronically excited states, as well as the not so well known vibration-electronic (V-E) energy transfers [4]. Only single quantum transitions, which are the most likely ones, have been considered in the V-V and V-T collisional exchange processes, with the exception of V-T exchanges in  $N_2$ -N and  $H_2$ -H collisions, in which multiquantum transitions are known to be important.

An accurate determination both of the EEDF and of the VDF of  $N_2$  ground-state molecules is absolutely crucial in order to obtain physical insight and meaningful results from modeling. The EEDF evidently determines all the electron transport parameters and the electron excitation



**Figure 1.** Calculated EEDF along the plasma column in pure  $N_2$ ,  $\omega/2\pi = 500$  MHz and  $p = 0.5$  Torr.



**Figure 2.** Calculated VDF of  $N_2(X^1\Sigma_g^+)$  molecules, for the same conditions as in figure 1.

rates describing the power transfer from the electrons to the heavy-particles. The VDF of  $N_2(X^1\Sigma_g^+, v)$  molecules is the main energy reservoir in nitrogen discharges and post-discharges, playing a central role in the all problem and establishing a strong link between the different kinetics [1, 2, 4]. As an example illustrating the coupling between the electron and vibrational kinetics, figures 1 and 2 show the variations of the EEDF and of the VDF of  $N_2(X^1\Sigma_g^+)$  molecules along the discharge, respectively, for a pure nitrogen discharge at  $p = 0.5$  Torr,  $\omega/2\pi = 500$  MHz

and  $R = 2.25$  cm. In order to unify the results, the distance towards the end of the column,  $z$ , is normalized to the total discharge length  $L_t$ . It is seen that the electron-molecule energy exchange processes influence significantly the EEDF shape. The observed decrease in the energy interval 1.5-3 eV as is well known and reflects the rapid rise of the vibrational cross-sections in this energy range. This effect of the "vibrational barrier" is well pronounced close to the end of the discharge, but is partly attenuated by superelastic collisions towards the surface-wave launcher, due to the higher degrees of ionization, and thus higher vibrational excitation in this region. The degree of ionization, for the conditions considered here, varies from approximately  $10^{-5}$  to about  $10^{-6}$  close to the plasma column end.

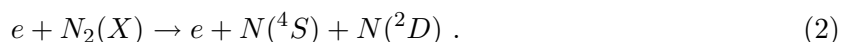
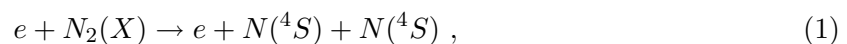
Different regimes of population and depopulation of the vibrational levels can be identified from the shape of the VDFs. The VDF shape results from the combined effects of e-V and V-V exchanges at low vibrational levels, of near resonant V-V exchanges at intermediate levels, which tend to form a plateau in this region, and to the simultaneous effects of vibrational dissociation and V-T exchanges at the highest levels. For the relatively low degrees of ionization corresponding to this case, the regions corresponding to the above mentioned mechanisms can be clearly identified in figure 2. There is small increase in the population of the high vibrational levels ( $v > 35$ ) towards the column end. Notice that the V-T rates associated with  $N_2$ -N collisions increase with the  $v$ -th quantum number by several orders of magnitude at constant gas temperature,  $T_g$ , and increase also as  $T_g$  increases. On the one hand, the simultaneous effects of the decrease in degree of ionization and gas temperature towards the column end cause a decrease in the population of the lower vibrational levels towards the end. On the other hand, the decrease of the nitrogen atom density and  $T_g$  towards the column end then causes an increased population of the higher vibrational levels ( $v > 35$ ) close to the discharge end, as a result of the decreasing influence of V-T depopulation mechanisms in  $N_2$ -N collisions.

### 3. Dissociation kinetics

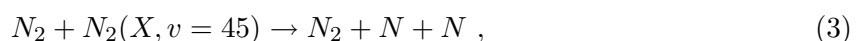
The study of dissociation processes in molecular gases is of major importance in several plasma based applications, such as metallic nitriding, surface treatments and microelectronics, since  $N(^4S)$  and  $H(1s)$  atoms are the most important active species for those applications. Furthermore, the degree of dissociation strongly influences the global discharge behavior, due to the interplay between different kinetics. It is worth to take some time to discuss the specificities of dissociation in each of the discharges under consideration, corresponding to pure  $N_2$ ,  $N_2$ -Ar and  $N_2$ - $H_2$  plasmas.

#### 3.1. $N_2$ discharges

May be a bit surprisingly, dissociation in pure nitrogen discharges is still an open and very interesting problem nowadays. A recent review of the issue has been presented in [4]. Dissociation in nitrogen occurs by direct electron impact,



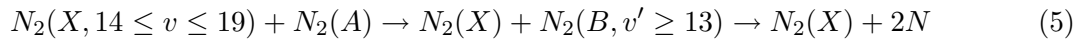
These two reaction are dominant and can explain the dissociation degrees experimentally observed for the conditions considered in the present paper. However, at pressures above  $\sim 1$  Torr, relatively low ionization degrees and lower reduced electric fields than those found in this study, dissociation by electron impact is not enough to provide the dissociation degrees found in a real discharge. Hence, additional sources of dissociation are required to explain the measured concentrations of nitrogen atoms. Vibrational dissociation from the last bound level into a pseudo-level in the continuum,



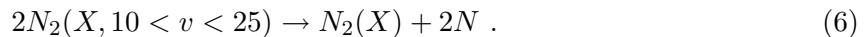
is not effective, due to the depopulation of the VDF in the high  $v$ -levels. Moreover, and contrary to what happens in  $N_2$ -Ar mixtures (see below), dissociative recombination of  $N_2^+$  ions,



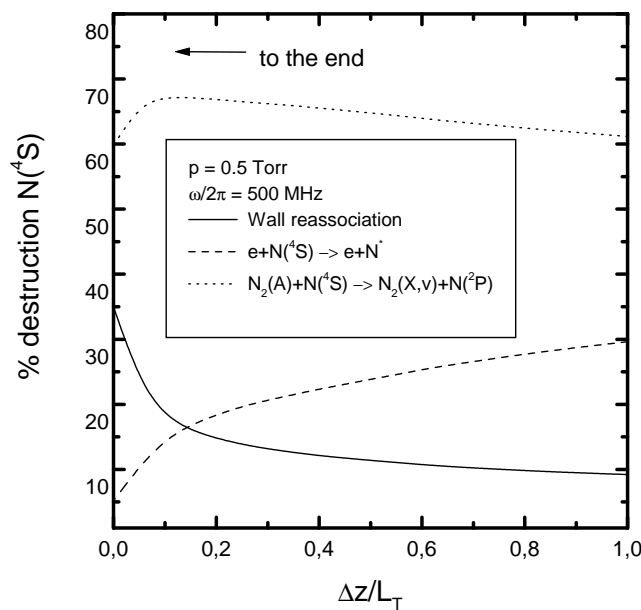
is not very effective in pure nitrogen, at least for relatively low ionization degrees. Thus, new mechanisms have been proposed, namely



and

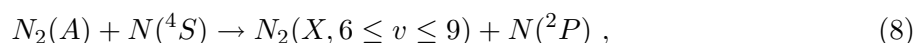
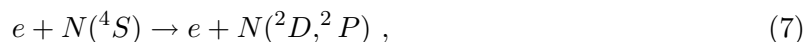


These two reactions seem capable of reproducing the available experimental data, but further investigation is required in order to clarify the subject.



**Figure 3.** Fractional contribution of the different  $N(^4S)$  destruction mechanisms, for the same conditions as in figure 1.

The rate of dissociation is controlled as well by the following reactions destroying  $N(^4S)$  atoms:



The contribution of these three mechanisms to the total destruction rate of  $N(^4S)$  atoms is shown in figure 3, for a microwave discharge in pure nitrogen at  $p = 0.5$  Torr and  $\omega/2\pi = 500$  MHz. Reactions (7) and (8) present by far the highest rates for destruction of  $N(^4S)$  atoms. However,

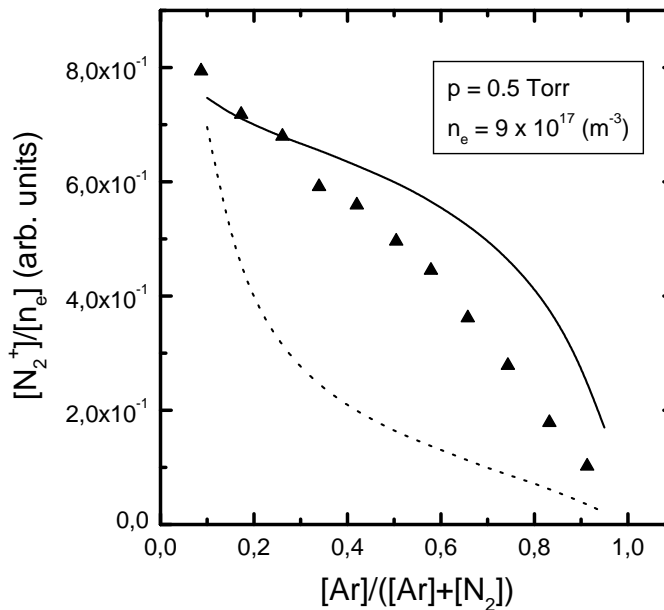
as discussed in [3], they do not constitute effective  $N(^4S)$  destruction mechanisms. Actually, most of the metastable atoms  $N(^2D, ^2P)$  formed in these reactions are reconverted back to ground-state atoms, as a result of electron superelastic collisions and quenching in volume and at the wall. Recombination at the wall (9) plays thus a very important role in the control of the population of nitrogen atoms in the discharge, even if its absolute destruction rate is much lower than those of the other reactions.

### 3.2. $N_2$ -Ar discharges

At high ionization degrees, there is a change in the dissociation balance when Ar is introduced into a nitrogen discharge. As the Ar content in the discharge increases, the production of nitrogen atoms by dissociative recombination through reaction (4) gradually increases, this channel becoming the dominant mechanism of production of  $N(^4S)$  atoms in the discharge. What happens is that the charge transfer reactions

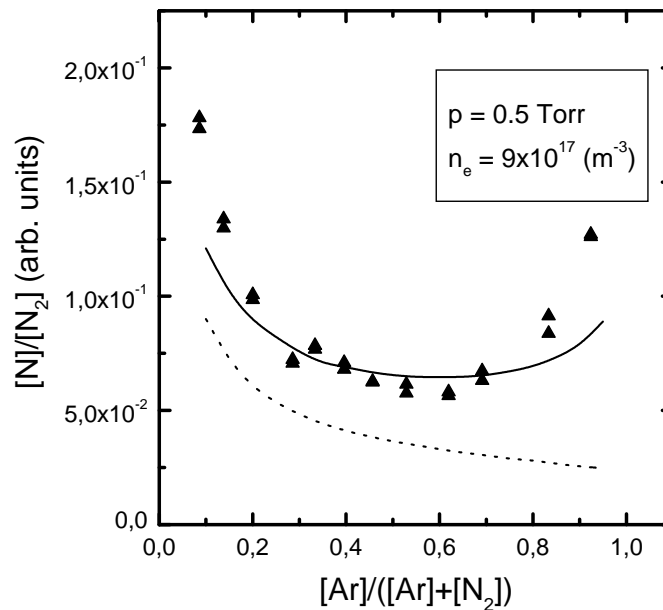


are very fast, and slightly more efficient on the forward direction than on the backward one. As a result,  $N_2^+$  ions are the dominant positive ions in the discharge, even for Ar contents as high as 90%, subsequently dissociating into two nitrogen atoms [7, 5].



**Figure 4.**  $N_2^+$  relative concentration as a function of Ar percentage, for a discharge operating at  $\omega/2\pi = 2.45$  GHz and  $p = 0.5$  Torr, by including (—) and neglecting ( $\cdots$ ) reaction (10). The experimental points were taken from [7].

To clarify this effect, figures 4 and 5 show the relative concentrations of  $N_2^+$  ions and  $N(^4S)$  atoms, respectively, as a function of the Ar composition, for a  $N_2$ -Ar discharge operating at  $\omega/2\pi = 2.45$  GHz,  $p = 0.5$  Torr, in a quartz tube with inner radius  $R = 0.75$  cm. The calculations have been performed by considering (full curves) and neglecting (dotted curves) reactions (10) and compared to the relative measurements reported in [7]. The calculations



**Figure 5.**  $N(^4S)$  relative concentration as a function of Ar percentage, with the same notation as in figure 4.

were made at constant electron density,  $n_e = 9 \times 10^{17} \text{ m}^{-3}$ , corresponding to the experimental conditions of the measurements, which were performed close to the launcher ( $\Delta z/L_t \simeq 1$ ). As it is clearly seen, an accurate calculation of the  $N_2^+$  ion population requires the inclusion of the charge transfer reactions (10). In addition, the concentration of  $N_2^+$  ions reflects on the degree of dissociation, due to the importance of dissociative recombination (4). For the conditions of figures 4 and 5, only electron impact dissociation and dissociative recombination are important sources of  $N(^4S)$  atoms. The contribution of dissociative recombination to the total dissociation rate raises from about 20% in a mixture containing 10% of Ar to 90% in a 5% $N_2$ -95%Ar. Other more subtle details, such as the influence of gas pressure in the behavior of  $N_2$  dissociation with Ar content, have been investigated in [7, 5].

### 3.3. $N_2$ - $H_2$ discharges

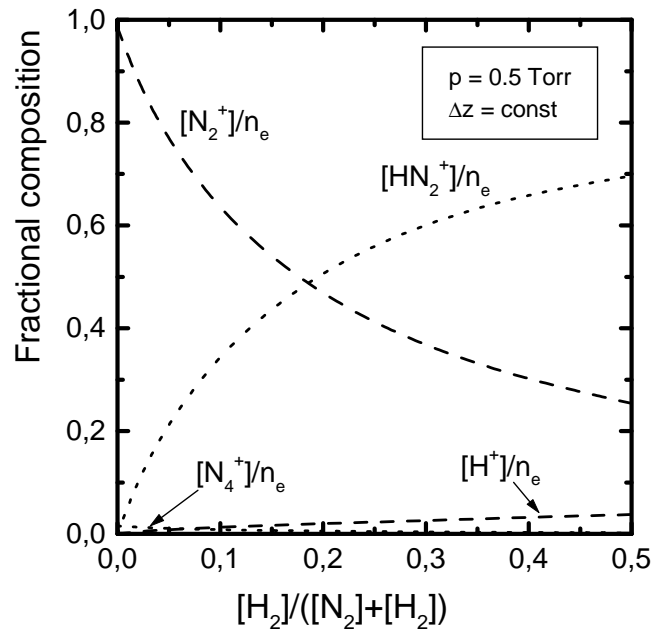
We have just seen that in microwave discharges in  $N_2$ -Ar mixtures the mechanisms of creation and loss of nitrogen atoms are the same as in pure nitrogen, although the relative importance of the different channels is dramatically affected. The study of  $N_2$  dissociation in  $N_2$ - $H_2$  mixtures becomes much more complex, because some additional mechanisms both of production and of destruction of nitrogen atoms take place.

From the side of production, a very important additional source is electron-ion recombination via



This reaction takes place not only in the gas phase, but mostly occurs during the surface neutralization of  $HN_2^+$  ions. According to our modeling results, this later process becomes the dominant mechanism of formation of  $N(^4S)$  atoms when the hydrogen fraction in the mixture increases. As a matter of fact, in this case  $HN_2^+$  ions form the dominant ionic species, as a result of the charge transfer reactions





**Figure 6.** Fractional ionic composition as a function of H<sub>2</sub> percentage, for the same discharge conditions as in figure 4.



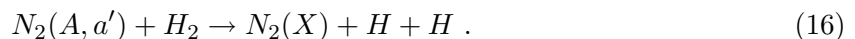
subsequently leading to the formation of N atoms in reaction (11). Figure 6 shows the calculated fractional ionic composition of the plasma as a function of the H<sub>2</sub> percentage in the mixture, at constant axial distance relative to the launcher (*i.e.*, at nearly constant electron density), for a discharge operating at  $\omega/2\pi = 2.45$  GHz,  $p = 0.5$  Torr, in a quartz tube with inner radius  $R = 0.75$  cm, confirming HN<sub>2</sub><sup>+</sup> as the dominant ionic species.

Looking now at the destruction channels of N atoms, two new mechanisms exist, involving the formation of NH:



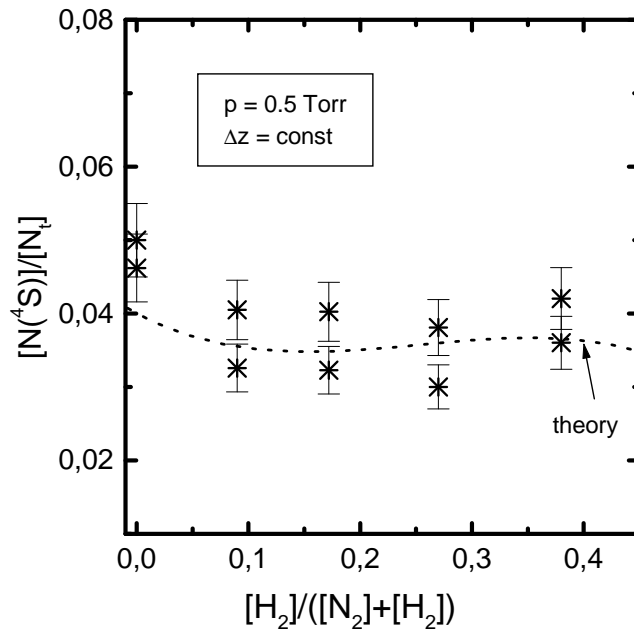
The concentration of N(<sup>4</sup>S) atoms calculated taken into account all its creation and destruction mechanisms is shown in figure 7, for the same conditions as in figure 6. The experimental data is taken from [10], where the rich behavior of nitrogen dissociation with pressure is studied as well. The good agreement between the model predictions and the measurements points towards the correctness of the present analysis.

It is still interesting to look at hydrogen dissociation, represented in figure 8 as a function of H<sub>2</sub> percentage, for the same conditions as in the previous figures. The degree of dissociation  $[H(1s)]/[H_2]$  remains practically constant for mixture compositions containing between 10 and 50 % of hydrogen. This is a result of a competition between the two most important channels of H<sub>2</sub> dissociation, electron impact dissociation, and dissociation of H<sub>2</sub> in collisions with metastable N<sub>2</sub>(A <sup>3</sup>Σ<sub>u</sub><sup>+</sup>) and N<sub>2</sub>(a' <sup>1</sup>Σ<sub>u</sub><sup>-</sup>),

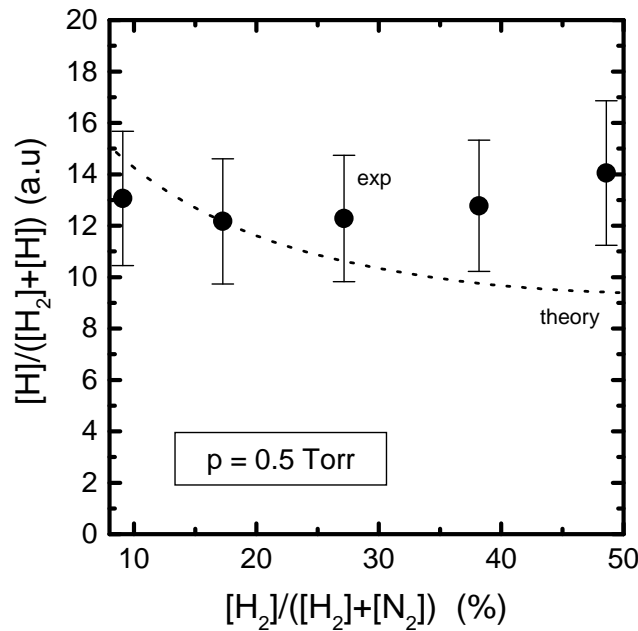


When hydrogen is added into a nitrogen discharge, the contribution of the first channel increases, since the EEDF is more populated at high energies [10]. On the other hand, H<sub>2</sub> dissociation





**Figure 7.**  $N(4S)$  atom density relative to the total gas density as a function of  $H_2$  percentage, for the same discharge conditions as in figure 4. The experimental points are from [10].



**Figure 8.**  $H_2$  dissociation degree as a function of  $H_2$  percentage, for the same discharge conditions as in figure 4. The experimental points are from [10].

in collisions with the nitrogen metastables  $N_2(A\ ^3\Sigma_u^+)$  and  $N_2(a'\ ^1\Sigma_u^-)$  decreases, simply as a consequence of the lower concentration of  $N_2$  in the mixture. The net result is the almost

constant dissociation degree of H<sub>2</sub> exhibited in figure 8.

#### 4. Conclusions

In this paper it is shown how self-consistent modeling, complemented with experimental campaigns, can be used as a powerful tool to investigate the elementary kinetic processes taking place in gas discharges and to gain physical insight into the basic phenomena ruling the discharge. Special attention has been paid to the dissociation mechanisms in N<sub>2</sub>, N<sub>2</sub>-Ar and N<sub>2</sub>-H<sub>2</sub> plasmas created in a microwave surface-wave sustained discharge.

Dissociation in pure nitrogen discharges is still not completely understood. Nevertheless, for the conditions of the present study, corresponding to low-pressure microwave discharges, N<sub>2</sub> dissociation occurs essentially by electron impact. The dissociation channels in N<sub>2</sub>-Ar mixtures are the same as in pure nitrogen. However, dissociative recombination  $e + N_2^+ \rightarrow N + N$  becomes the most important process of creation of N atoms when the Ar content in the mixture increases, as a consequence of a very efficient charge transfer process from Ar<sup>+</sup> ions to N<sub>2</sub><sup>+</sup>,  $Ar^+ + N_2 \rightarrow Ar + N_2^+$ . In N<sub>2</sub>-H<sub>2</sub> discharges a very important contribution to nitrogen dissociation is the electron-ion surface recombination of HN<sub>2</sub><sup>+</sup> ions, which forms NH and N(<sup>4</sup>S) atoms, since this ionic species is efficiently formed in the charge transfer reactions  $N_2^+ + H_2 \rightarrow HN_2^+ + H$  and  $H_2^+ + N_2 \rightarrow HN_2^+ + N$ . The degree of dissociation of H<sub>2</sub> remains essentially constant for H<sub>2</sub> percentages ranging between 10% and 50%, as a net result of the competition between two H<sub>2</sub> dissociation channels with opposite behaviors with the mixture composition,  $e + H_2 \rightarrow e + H + H$  and  $N_2(A, a') + H_2 \rightarrow N_2(X) + H + H$ .

Surface processes play a very important role in this type of discharges and should be studied in detail in the future. Firstly, the probabilities for heterogeneous atomic recombination control to a big extent the atomic concentrations found in discharges in pure gases. Even if their rates of destruction of atoms are relatively low, other destruction mechanisms with higher rates often do not constitute effective destruction processes, as they form excited atoms which are later reconverted to ground-state. An important part of this reversion occurs at the wall, emphasizing the importance of plasma-wall interactions. Finally, in the mixture of nitrogen with other gases, electron-ion recombination at the wall may constitute the major production mechanism of N atoms in the discharge. This is the case with the neutralization of HN<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>+</sup> ions at the wall in N<sub>2</sub>-H<sub>2</sub> mixtures. Due to the interplay between different kinetics and the non-linearity of the discharge, by ruling the degrees of dissociation, surface processes have a strong influence in all the discharge physics.

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