Time resolved diagnostics and kinetic modeling of the ignition transient of a $\text{H}_2 + 10\% \text{N}_2$ square wave modulated hollow cathode discharge

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Abstract

Time resolved emission spectroscopy and quadrupole mass spectrometry are used for the experimental diagnostics of a low pressure (8 Pa) modulated dc hollow cathode discharge of $\text{H}_2 + 10\% \text{N}_2$. The time-dependent experimental results are reasonably accounted for by a zero order kinetic model developed in our group and checked previously with steady state measurements [Carrasco et al. 2011 *Phys. Chem. Chem. Phys.* **13** 19561], which is now validated under more stringent conditions. Besides the discharge precursors, which are partly recycled in wall reactions, NH_3 is produced in small but appreciable amounts. The slower evolution of NH_3 , as compared with H_2 and N_2 , is traced back to the multistep surface reaction mechanism responsible for its production. An analysis of the time variation of optical emission measurements shows that excited $\text{NH}(\text{c}^1\Pi)$ radicals are essentially formed in the electron impact dissociation of NH_3 .

1. Introduction

The fundamental study of low pressure plasmas of H_2 and N_2 mixtures has been stimulated by practical applications, such as ammonia synthesis [1-8] or metal surface nitriding [9-11]. Although iron is nitrided mainly by nitrogen atoms [12], the addition of small amounts of hydrogen in the gas mixture has beneficial effects in iron and austenitic stainless steel nitriding, giving as a result thicker nitrided layers [10,11] and an increased surface hardness [10]. Hydrogen seems to act as a reducer of the surface oxides [12], which would enhance atomic nitrogen diffusion [13]. In a similar way to ammonia synthesis in low pressure H_2 and N_2 plasmas, gas phase processes would supply the chemical active species necessary to favor surface mechanisms in plasma nitriding. As a consequence, a significant number of experimental studies have used spectroscopic diagnostics to identify gas phase excited species in plasmas of H_2 and N_2 mixtures as a function of the relative concentration of both precursor gases [4,5,10,11,14] and, in some cases, to determine the concentration of N, H and NH_x radicals [6,8,15]. One common observation is the increase in atomic N(H) density if a small percentage of $\text{H}_2(\text{N}_2)$ is added to a $\text{N}_2(\text{H}_2)$ plasma [9,11,14]. Theoretical models [16,17] show

the modification of the electron energy distribution function (EEDF) of the pure plasma when a second gas is introduced. In addition, a strong coupling of excitation, ionization, electron energy distribution and vibrational excitations in these plasmas is obtained [14,16,17], making difficult the determination of the preferential processes in each case. This complexity increases when surface processes need to be added to the gas-phase kinetics to explain the global experimental results [5].

With the aim of elucidating the detailed kinetics, pulsed discharges are considered helpful [4,18] since specific plasma processes occurring at different rates can be evinced by adjusting the duration of the pulses. Besides, N₂-H₂ dc pulsed discharges could be advantageous in plasma nitriding for several technical reasons [13,19,20], which also stimulates their study. In these respect, spectroscopic techniques are used for the analysis of these plasmas, not only due to its non-intrusive character but, also, because of its good spatio-temporal resolution. Williamson et al. [21] measured the atomic hydrogen production by two-photon absorption induced fluorescence (TALIF) as a function of pulse duration and concentration of N₂ in H₂-N₂ plasmas. They showed how the H-atom signal was enhanced with increasing N₂ concentration only for relatively long discharge pulses ($\geq 500 \mu\text{s}$). Vibrationally excited H₂ and N₂ were considered responsible for this increase that would be induced by heavy-particle energy transfer, as opposed to the H-atom production by direct electron impact dissociation of H₂ characteristic of shorter pulses. However, the effects of modifying the relative concentration of one of the components in the discharge mixture are not restricted to neutral species and also influence ions [10,20,22]. By using optical emission spectroscopy (OES) and laser induced fluorescence (LIF) in both dc and dc-pulsed discharges, Scherentz et al. [22] showed in N₂-H₂ glow discharges that the influence of H₂ on the density of N₂⁺ depended on the electronic level of the ion. Whereas the ion ground state N₂⁺(X²Σ_g⁺) was neutralized by H₂, the N₂⁺(B²Σ_u⁺) electronic excited state was not affected. Progressively higher experimental knowledge is necessary to improve theoretical models, which require an integration of gas-phase volume reactions and surface processes [5], in order to get a deeper knowledge of the physics and chemistry taking place in the plasma and in the plasma-surface interface, still not fully understood.

In previous publications, the authors have demonstrated how the employment of modulation techniques facilitates the distinction among processes, relevant in different time scales, for N₂O [23,24], NO₂ [25] and air plasmas [26]. Time-resolved spectroscopy for the observation of molecular [23,24] or atomic species [25,26] in combination with kinetic modeling of the modulated discharges allowed to clarify the most important reactions [23,24] or the estimation of rate coefficients [26] in those plasmas. In this work, a similar procedure is followed to get further details in H₂ + 10% N₂ plasmas by using low frequency modulation, together with a recently developed kinetic model [8] that accounted quite satisfactorily for

stationary state results. Emission spectroscopy is used, on the one hand, for the detection of excited radicals (NH_x) and atoms (H, N) previously advanced to be present in the H_2/N_2 discharges [8]; and, on the other hand, to analyze the evolution of the concentrations of neutrals and ions during the transient from plasma ignition till the attainment of the steady-state. Mass spectrometry is employed also to obtain complementary measurements of the temporal evolution of N_2 and NH_3 . These experimental results are compared with the time resolved concentrations of the different species obtained by the mentioned zero-order kinetic model [8], which is now employed for analyzing their transient behaviour. The comparison between experiment and calculations is used to assess the global validity of the model and to introduce refinements where needed.

2. Experimental

The description of the plasma reactor has been given in previous works [27,28]. It consists of a grounded cylindrical stainless steel vessel (10 cm diameter, 34 cm length) and a central anode, which is pumped to a base pressure of 10^{-4} Pa by a 450 l/s turbomolecular pump and a dry pump. The reactor chamber has different ports for connection of gas inlets, pressure gauges, optical windows and plasma diagnostics tools. Measurements are done under continuous flow conditions. The absolute pressures of the gas precursor mixtures (measured by a capacitance manometer Leybold CTR90) are regulated by balancing the gas flow with two needle valves at the entrance (one for each gas) and a gate valve at the exit of the reactor. Mixtures of H_2 (90%) and N_2 (10%) were used for a total reactor pressure of 8 Pa. A differentially pumped vacuum chamber (base pressure 10^{-6} Pa) is connected to the plasma reactor through a 100 μm diaphragm, where a mass spectrometer Balzers QMG220 is mounted for analysis of the molecular gases during the plasma measurements (at a total pressure $\sim 10^{-5}$ Pa), with a secondary electron multiplier working in analog mode as detector. The mass spectrometer signals have been calibrated following the procedure described in [8] in order to fix the initial proportion of the gas mixtures and, moreover, to determine the relative depletion of N_2 and H_2 during the discharge, and the concentration of NH_3 that is generated in the plasma.

A DC power supply built in our laboratory was used to feed the discharge. Plasma currents $I_p \sim 150$ mA and supplied voltages ~ 350 V were sustained during the experiments. For the time-dependent measurements, the discharge was externally modulated at 0.025 Hz (47.5% duty cycle) by means of a SRS DG535 square wave generator. This frequency was selected in such a way that the steady-state concentrations of the chemical species were reached both during the discharge on and off half-periods of each cycle. An electron gun built in our laboratory (consisting basically of a floating tungsten filament, 130 μm diameter, fed by a low voltage DC power supply, which can be polarized up to -2000 V for efficient extraction of the

electrons) was required for the ignition of the plasma at the low pressures employed in this study. The modulated measurements were done at a continuous filament current of ~ 2.1 A and without polarizing the electron gun at high voltage in order to minimize possible plasma perturbations. No differences in the spectrometric measurements were detected during continuous DC discharges with the electron gun turned on and off, and thus plasma modifications by the electron source are considered negligible.

Complete emission spectra of the plasmas have been recorded in the 300-800 nm wavelength range during continuous discharge operation with pure H_2 and pure N_2 discharges, and with the H_2+N_2 mixture for the identification and assignment of the lines of interest. The light from the discharge is transmitted by an optical fibre, imaged on the entrance slit of a JovinYbon HORIBA FHR1000 spectrometer (Czerny-Turner configuration, grating 1800 nm^{-1} and focal length 1m), and detected by a front exit SYNAPSETM CCD camera (1024 x 512) with a resolution of 0.025 nm for an input slit width of 25 μm . Individual transitions, corresponding unequivocally to different neutral (N_2 , H_2 , NH and H) or ionic species (N_2^+) observed in the plasma, have been selected for the time evolution studies during the modulated discharge cycles. For the time resolved emissions, the maximum intensity of each spectral line has been detected with a side exit photomultiplier Hamamatsu connected to a home-made analogue multiplier (Gain: 10^6 V/A, Time constant: 65 ms), whose output is registered by a digital oscilloscope YOKOGAWA DL708E at digitizing sampling intervals of 10 ms.

The oscilloscope acquisition is triggered 50 ms before the ignition of the discharge by a reference pulsed signal coming from the SRS DG535 square wave generator. The emission signal and the time evolution of the modulated plasma current are simultaneously recorded on different channels of the oscilloscope. For the improvement of the signal to noise ratio, each selected spectral transition has been averaged over 8 or 16 modulation cycles. These measurements have been taken at a spectral resolution of 0.075 nm (input and exit slits of 200 μm), in order to get significant intensities and prevent possible changes in amplitude due to slight drifts in the wavelength position during acquisition. It was verified that the selected transitions did not overlap with neighbouring spectral lines.

The electron mean temperature, T_e , and total charge density, n_e , in the reactor are obtained from the analysis of the characteristic curves of the double Langmuir probe measurements of the continuous discharge at the corresponding total pressure of the mixture [8]. The approximation of orbital limited motion in a collision-free probe sheath is considered to be fulfilled [29].

3. Kinetic model

Briefly, the zero order kinetic model [8] consists of a set of time resolved coupled differential equations whose solution describes the time evolution of neutral (H, N, NH, NH₂ and NH₃) and ionic species (H⁺, H₂⁺, H₃⁺, N⁺, N₂⁺, NH⁺, NH₂⁺, NH₃⁺, NH₄⁺ and N₂H⁺) from the plasma ignition to the attainment of the steady state. The model comprises gas phase and surface chemistry. The gas phase processes consider electron impact ionization, dissociation, neutralization and ion-molecule reactions for precursors and products. The surface processes include ion neutralization at the reactor walls and heterogeneous reactions among the neutral species. NH₃ is produced via plasma-surface interactions by the successive hydrogenation of adsorbed nitrogen atoms and hydrogen containing radicals at the surface of the stainless-steel reactor walls, following the reaction scheme of references [5,8]. The free plasma electrons are assumed to follow a Maxwellian-like energy distribution function.

The steady state results of the mass spectrometric measurements for the stable species (H₂, N₂ and NH₃) before and after the ignition of the discharge are represented in Figure 1, together with the corresponding model predictions for neutral plasma species. Note that the distribution of molecules in the plasma is well accounted for by the model, which provides also the concentrations of atoms and radicals.

It should be emphasized that, for some parameters and assumptions introduced in the model for our stationary state study, in particular for those related with heterogeneous reactions leading to NH₃ formation and H₂ and N₂ recycling in the wall, no previous data were found in the bibliography. On the other hand, model simulations can lead to appreciable changes in the time evolution of plasma species with relatively small variations in some of the parameters, which have little influence on the steady state distributions. A comparison of experimental transient data with theoretical predictions should thus allow an assessment of the model under more stringent conditions.

4. Results and discussion

Figure 2 shows the mass spectrometric time evolutions of N₂ and NH₃ signals produced in the modulated discharge of H₂ + 10% N₂ at 8 Pa (thin solid lines), together with the theoretical predictions (thick solid lines) of the kinetic model explained in detail in [8]. The experimental data have been scaled for each species to the absolute values provided by the model. The input parameters and rate coefficients of the model used in Figure 2 are the same as in [8] (as well as in Figure 1): electron temperature, T_e=2.8 eV, electron density, N_e=3.3 × 10¹⁰ cm⁻³, a residence time of 0.61 s and a gas temperature of 300 K. Zero surface covering before ignition and a site saturation value of 10¹⁵ cm⁻² were also assumed, in agreement with [8,30].

Different experimental time evolutions are observed for N_2 and NH_3 . The N_2 concentration drops fast and reaches a shallow minimum approximately one second after the ignition of the discharge. Beyond this non-pronounced minimum, the concentration of N_2 rises slightly and reaches its steady state. In contrast, the concentration of NH_3 rises monotonically, at a slower pace, and reaches later its steady state. The model accounts reasonably well for the measured N_2 behaviour, but the predicted NH_3 rise is faster than that experimentally observed. The mass spectrometric technique could not be used for time resolved measurements of H_2 concentrations due to the large pump-out times ~ 5 s for this gas in the detection chamber, whose turbomolecular pump had a poor compression factor. For the heavier species, the pump-out times were much smaller and were hardly expected to interfere with the measurements. In any case, we have used visible/UV emission spectroscopy of excited plasma species in order to circumvent any problem associated to the mass spectrometric detection. Optical emission spectroscopy is free from the just described instrumental time delays and provides also additional information on excitation and dissociation processes in the plasma.

The emission spectra of the low pressure H_2 - N_2 plasmas under study are characterized by a richness of transitions where the most prominent lines of the second positive system of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$), the first negative system of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$), the Fulcher- α band of H_2 ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) and the Balmer lines of atomic H are easily identified. With much smaller intensity, transitions corresponding to atomic N are observed at 744.2 nm ($3p^4S_{3/2}^0 \rightarrow 3s^4P_{3/2}$) and 746.8 nm ($3p^4S_{3/2}^0 \rightarrow 3s^4P_{5/2}$) [31]. Transitions corresponding to N^+ at 566.67 nm ($3p^3D_2 \rightarrow 3s^3P_1^0$) and at 567.96 nm ($3p^3D_3 \rightarrow 3s^3P_2^0$) [31] are also detected. Regarding the identification of radicals, the (0-0) vibrational band of $NH(c^1\Pi \rightarrow a^1\Delta)$ and the (0-0) and (1-1) vibrational bands of $NH(A^3\Pi \rightarrow X^3\Sigma^-)$ are observed in the 324-345 nm region of the emission spectrum. Figure 3 shows the part of the c-a system of NH which is free from overlapping with the A-X system. The line assignments of the c-a system are based on [32] (with wavelengths corrections for air). The optical emission from NH_2 radicals ($\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$) was not detected.

The time evolution of emission signals pertaining to H_2 and N_2 molecules are represented in Figure 4. Emissions associated to NH_3 will be discussed below. Figure 4a displays the time-resolved emission from the Q1 rotational line at 622.48 nm belonging to the Q-branch of the (2-2) band of the H_2 Fulcher- α system ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$ electronic transition) [33]. The N_2 time-resolved signal at 375.54 nm, corresponding to the transition ($v'=1, v''=3$) of $C^3\Pi_u \rightarrow B^3\Pi_g$, can be seen in Figure 4b. For an ideal perfectly square modulation of the discharge current (with instantaneous turn-on, without surpassing the steady-state current), emission signals of both precursors should have a fast rise immediately after the discharge is ignited, as a result of their electronic excitation, since H_2 and N_2 can be considered still hardly dissociated at

this moment and, afterwards, these emissions should display a slower decrease due to H_2 and N_2 dissociation, until reaching steady-state conditions. However, Figure 4c shows the true modulated plasma current record. An initial overshoot of the current signal is appreciated, with a rise time of few milliseconds and a settling time of around 60 milliseconds. Although this overshoot is reflected in all the time-resolved emission signals by the introduction of a spike superimposed on the expected emission records, it does not seem to perturb seriously the subsequent data or preclude the comparison with the model. On the other hand, it should be noticed that, logically, these spikes are not recorded in the evolution of the N_2 and NH_3 relative concentrations detected by mass spectrometry (Figure 2). Moreover, the fast response of the emission spectroscopic system is just verified by the detection of these spikes.

After the initial spike coinciding with the discharge turn-on, H_2 emission shows a constant behaviour (Figure 4a). Unlike H_2 , the emission of N_2 (Figure 4b) goes through a shallow minimum at approximately 0.5 s from the beginning of the discharge and, afterwards, reaches a steady-state value around 2.5 s later. Equivalent results have been obtained for transitions between different vibrational levels of the same N_2 system (for example, $(v'=0, v''=1)$ at 357.69 nm). On Figure 4a, the time evolution of the H_2 concentration predicted by the model [8] (dashed line) is also shown. The calculated H_2 concentration presents an appreciable minimum very shortly after the ignition of the discharge, which is not detected experimentally. The minimum in the model calculations can be traced back to the assumption of initial “zero coverage” of the reactor walls, and can be corrected by considering a non-zero concentration of adsorbed H atoms at the beginning of the discharge. An initial H atom concentration of $7 \cdot 10^{14} \text{ cm}^{-2}$, quite realistic for the experimental conditions of our measurements, is introduced to remove the minimum from the simulated H_2 time evolution (see Figure 4a). With this correction the H_2 concentration is predicted to reach its steady state in less than 100 ms, in accordance with the observations. The correction has no influence either in the steady state concentrations or in the time evolution of N_2 or NH_3 , and is included in the rest of the model results presented in this paper. The calculated N_2 evolution is also represented in Figure 4b. Also in this case the model can largely account for the experimental behaviour and, in particular, for the very shallow minimum observed, but the simulated minimum is shifted by about 0.5 s toward longer times. This discrepancy at short times might be related, at least partially, with the higher electron densities (and possibly electron temperatures) associated with the initial spike in the discharge current.

Transitions at 563.8, 564.1 and 567.2 nm are observed in the discharges of H_2 and N_2 mixtures, which are not present in discharges of pure H_2 and N_2 . They are assigned to NH_3 , according to [34]. Although the diffuse Schuster band with maxima at 567.2 nm and 563.9 nm (observed for first time by Schuster [35] in ammonia discharges and identified with this

compound) was assigned to NH_4 by Herzberg [36], the reassignment to the electronic transition $\tilde{\text{C}}' ^1\text{A}_1 \rightarrow \tilde{\text{A}}' ^1\text{A}_2''$ of ammonia seems to be consistent [37]. However, the observed transitions are too weak to perform time-resolved emission spectroscopy. Despite this circumstance, time-resolved emission corresponding to rotational transitions of the (0-0) vibrational band of NH ($\text{c}^1\Pi \rightarrow \text{a}^1\Delta$) can be used to follow the time evolution of ammonia as we shall show in the following. The (c—a) emission system has been, in fact, observed both in the electron impact dissociation [38-40] and in the photofragmentation [41,42] of NH_3 , and although the dissociation dynamics is not known in full detail, it has been attributed to an optically allowed transition [40,42]. The energetic threshold is close to 9.8 eV [42]. Nevertheless, additional contributions from the direct excitation of NH and from the dissociation of NH_2 by electron impact need to be discussed. Firstly, direct electron impact excitation to NH ($\text{c}^1\Pi$) from the triplet ground state ($\text{X } ^3\Sigma^-$) of NH corresponds to a forbidden transition. The transition, if present at all, would be very weak and this contribution can be ruled out in principle. Secondly, $\text{NH}(\text{c}^1\Pi)$ could also be generated in the electron impact fragmentation of NH_2 . The c—a transition was also found in NH_2 photodissociation experiments [43], but in that work the analysis was focused on the formation of $\text{NH}(\text{A } ^3\Pi)$ and, as far as we know, no additional direct experimental evidence for this process is available in the literature. The energetic threshold for the production of NH ($\text{c}^1\Pi$) from the ground state of NH_2 is close to 10 eV [44] and thus similar to that found in NH_3 . Although the high density of NH_2 Rydberg states in the region above 9 eV is expected to lead to a complex dissociation dynamics [44], the details are again not known. Therefore, transitions from the c—a system of NH could, in principle, proceed both from the electron dissociation of NH_3 and of NH_2 . In this respect, the kinetic model can give some hints, since it determines the concentration of the NH and NH_2 radicals as well as NH_3 and their changes during the ignition of the discharge.

Figure 5 shows the time-resolved emission for the Q(6) rotational transition of the $\text{c}^1\Pi_{v'=0} \rightarrow \text{a}^1\Delta_{v''=0}$ system of NH at 326.18 nm. Additional measurements were done at 325.63 nm Q(4) and 325.88 nm (Q(5)+R(13)+P(2)) in order to check that the evolution with time of the emission signal is independent of the selected rotational transition. The observed evolution is much slower than those observed for N_2 and H_2 , and is consistent with the behaviour expected for a compound not present initially in the reactor but formed during the discharge operation. The calculated evolutions of NH, NH_2 and NH_3 , which are the possible sources of excited NH, are also represented in Figure 5. The final concentrations of NH and NH_2 are different from that of NH_3 but the signals have been normalized to the same steady-state value for comparison. Although none of the calculated curves matches exactly the evolution of the NH emission, the predicted NH_3 concentration as a function of time is much closer to the measurement than those of NH_2 and NH. Both the calculation and the selection rule mentioned above indicate that a

contribution to NH emission from the direct excitation of NH is very unlikely and, although a contribution from the electron impact dissociation of NH₂ cannot be entirely discarded, the calculated curves support that NH ($c^1\Pi$) is chiefly originated in the electron impact fragmentation of ammonia, in good agreement with [38-40]. A comparison with the results from mass spectrometry displayed in Figure 2 supports further this assignment. Both, the NH optical emission and the NH₃ mass spectrometric signal show a comparatively slow rise and reach their steady state concentrations more than three seconds after the ignition of the discharge. The calculated NH₃ evolution predicts also a faster rise than that of the measured signals during the first two seconds and this is more apparent in the case of the mass spectrometric results.

The reasonable agreement between the calculated and measured time evolution of the major species in the plasma corroborates further the adequacy of the set of mechanisms and rate coefficients used in the kinetic model [8]. In particular, the measurements validate the prediction of a relatively fast evolution of N₂ and H₂, which is determined by electron impact dissociation and by Eley-Rideal surface recycling, as compared with the slow buildup of NH₃, which is formed through a multistep surface mechanism involving both Eley-Rideal and Langmuir-Hinshelwood processes. The usual assumption of a saturation site density of $\sim 10^{15}$ cm⁻² [8,30] is also indirectly verified.

Time-resolved emission measurements of the transitions at 391.44 nm ($v'=0, v''=0$) and 427.81 nm ($v'=0, v''=1$) of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ system of N₂⁺ [45] were also recorded during the modulated discharges in order to analyze the evolution with time of this ionic species. The curves (not shown for brevity) follow a very similar evolution to N₂, in good agreement with the model, which considers the formation of N₂⁺ by direct electron impact ionization of N₂. Finally, the time-resolved emission of the H _{α} transition ($3d\ ^2D \rightarrow 2p\ ^2P_0$) at 656.28 nm was also measured and found to be similar to that of H₂, which points to dissociative excitation of the H₂ major precursor as the main source of this emission. Data from a recent model by Lavrov et al. [46] suggests that there should be an appreciable contribution of direct H excitation to this emission which, according to the model predictions, would result in a slower evolution; but this is not observed in our time resolved measurement.

5. Summary and conclusions

A square wave, low-frequency modulated, hollow cathode discharge of H₂ + 10% N₂ mixture has been characterized by mass spectrometry and visible/UV emission spectroscopy resolved in time. Emission spectroscopy has allowed not only the identification of stable neutral molecules (H₂, N₂ and NH₃) but also of highly reactive species (N and H atoms, N⁺ and N₂⁺ ions, and NH radicals) in the steady state discharge.

The time-resolved emission spectroscopic measurements validate the essential processes and parameters of the kinetic model previously developed in [8] and, in particular, the relatively slow multi-step mechanism for NH_3 production through heterogeneous wall reactions involving both Eley-Rideal and Langmuir–Hinshelwood mechanisms. The calculated steady state distributions of neutrals and ions, as well as the time scales in which these values are reached, are in reasonable agreement with the experimental results. The consideration of atomic H adsorbed at the surface before the ignition of the discharge, which is a sensible assumption for an experimental set-up subjected to repeated hydrogen discharges, improves the agreement of the model simulations with the measured evolution of H_2 .

Time resolved emission measurements provide also valuable information about the mechanisms of formation of excited atoms and radicals. In this respect, the correspondence between the time evolution of emission lines corresponding to transitions from the c—a system of NH and the calculated NH_3 formation indicates that, in the present discharge, excited $\text{NH}(\text{c}^1\Pi)$ is mainly formed by electron impact dissociation of ammonia and that other possible sources, like NH_2 or the direct excitation of NH should play at best a minor role.

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Figure captions

Figure 1. Relative concentrations of the neutral species before the ignition of the 8 Pa, $\text{H}_2 + 10\%$ N_2 discharge (dashed bars), and in the plasma steady state: Light grey bars indicate the mass spectrometric results for the stable species H_2 , N_2 and NH_3 in the plasma. Dark grey bars show the model predictions for neutral species, including radicals and atoms. The sum of the predicted H_2 , N_2 and NH_3 concentrations has been normalized to the sum of the measured relative concentrations of these species in the steady-state of the discharge.

Figure 2. Time-resolved evolutions of the relative concentrations of the N_2 precursor and of the NH_3 product from the ignition of the discharge until attainment of steady-state conditions, measured by mass spectrometry in the modulated $\text{H}_2 + 10\%$ N_2 discharge at 8 Pa, and the corresponding predicted concentrations given by the model of reference [8]. In this figure, the experimental signals (narrow lines) have been scaled individually for best fit to the predicted steady state results (thick lines).

Figure 3. Emission of the (0,0) vibrational band of the $\text{NH}(\text{c}^1\Pi \rightarrow \text{a}^1\Delta)$ system in a spectral region free from overlapping with other discharge emissions. The line assignments are based on [32].

Figure 4. Narrow lines: Time-resolved emission signal of (a) H_2 (measured through the Q1 spectral line of the Q(2-2) band of the Fulcher- α system) and (b) N_2 (measured through the ($v'=1, v''=3$) line of $\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$). (c) Time evolution of the modulated plasma current during and after the discharge ignition. The dashed line curve in (a) corresponds to the predicted concentration of H_2 according to the published model [8]. The solid lines in (a) and (b) show the calculated concentrations assuming an initial non-zero concentration of H atoms at the surface (see text for more details). In the case of N_2 , both predicted evolutions are coincident.

Figure 5. Evolution with time of the Q(6) transition of $\text{NH}(\text{c}^1\Pi_{v'=0} \rightarrow \text{a}^1\Delta_{v''=0})$ as recorded by emission spectroscopy, together with the time variations of NH_3 , NH_2 and NH concentrations predicted by the corrected model. The stationary concentrations of NH_2 and NH radicals are rescaled for comparison. The similitude of the calculated evolution of NH_3 and the NH experimental time-resolved emission record supports that NH is formed by the electron impact dissociation of ammonia. See text for more details.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5