Spectroscopic Study of NH_3-to-H_2 Conversion in an Ar-NH_3 Dielectric Barrier Discharge at Atmospheric Pressure

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Abstract: Penning gas mixtures are useful to sustain homogeneous dielectric barrier discharges (DBDs) at atmospheric pressure. For Ar-based DBDs, Penning reactions involving Ar metastable atoms and NH_3 can induce both ionization and dissociation. This work presents the results of a time-resolved optical emission spectroscopy study of the plasma chemistry in Ar-NH_3 DBDs. Using specific emission bands in the VUV and UV range, a method to record the NH_3-to-H_2 conversion is proposed.

Keywords: Dielectric Barrier Discharge, Penning mixture, Optical Emission Spectroscopy

1. Introduction

Penning gas mixtures are common in atmospheric pressure DBDs: they are made by adding a small amount of a gas (called quench gas) into a noble gas. The principle is to use a species whose ionization potential is lower than that of the first excited level of the noble gas. Thus, through quenching, the first excited state of the noble gas can ionize the quench gas, participating in the creation of the electronic avalanche. In this mechanism, the Penning mixture lowers the breakdown voltage with respect to the one of the nominally pure noble gas. This allows to obtain a homogeneous discharge at atmospheric pressure, avoiding inhomogeneous breakdowns and filamentary discharge regimes [1]. However, if the quench gas is a molecular gas, collisions with the excited state of the noble gas can induce both ionization and dissociation reactions. For example, in Ar-NH_3 gas mixtures, ionization of NH_3 by Ar($1s_3$) or Ar($1s_5$) (Ar metastable states in Paschen notation) occurs in 42% of cases, the rest of the time, a dissociation or dissociative excitation of NH_3 occurs [2]. Hence, because of NH_3 dissociation, the plasma chemistry in Penning gas mixtures can significantly change along the gas flow lines of the Ar-based DBD.

The aim of this work is to analyse the dissociation of NH_3 in low-frequency Ar-NH_3 glow DBD sustained at atmospheric pressure. Based on time-resolved optical emission spectroscopy in the VUV and UV range, a new method describing the NH_3-to-H_2 conversion is proposed.

2. Experimental setup

The discharge studied in this work is sustained in a square tube in a plane-plane configuration with top and bottom 4.7*0.2 cm² metallic electrodes covered by a 1 mm thick 6*0.4 cm² quartz plate. The side faces have the same dimensions as the quartz plates and are made of MgF_2 to let the UV-VUV photons escape the discharge zone. The gas gap is 2 mm. The pressure of Ar + 215 ppm of NH_3 is maintained at 750 Torr. In this work, the total gas flow rate varies from 97 to 420 sccm. For each condition, atmospheric pressure operation is maintained using a throttle valve coupled with a pumping system located at the outlet of the discharge tube. The bottom electrode is powered with a low frequency 50 kHz signal coming from a function generator (Tektronix AFG 3021B), an audio amplifier (Crest CC4000) connected to a bridged resistance, and a step-up voltage transformer (Atesys-Montoux). Top electrode is grounded. Electrical signals are recorded using a high voltage probe (Tektronix P6015A) and a current probe (Lilco LTD 13W5000). Both signals are visualized on an oscilloscope (Teledyne Lecroy HDO6104A). Time-resolved Optical Emission Spectroscopy (OES) measurements are recorded 2 cm after the entrance of the discharge using 2 different optical devices. The first one is a 1 m focal length monochromator (Mc Pherson 225) with a 1200 lines/mm grating connected to a photomultiplier tube (Hamamatsu R7311) for analysis of UV-VUV photons. The whole system is put under vacuum and the distance between the MgF_2 window and DBD is set to 1.2 cm (minimal distance allowed by the experimental setup) to minimize air absorption [3]. The second one is 0.32 m focal length monochromator (Princeton Instruments IsoPlane SCT-320) equipped with a 2400 lines/mm grating and an intensified charged coupled device (ICCD) camera (Princeton Instruments PI-MAX4 1024*256) for analysis of UV-visible photons.

3. Results and discussion

The discharge is powered at 50 kHz, 2.5 kV. In such conditions, the discharge is in a glow mode characterized by two short-current peaks (about 1 µs each) per period of the applied voltage (20 µs). Currents peaks as function of time are presented in Figure 1. The results are shown for different values of the total gas flow rate while maintaining atmospheric pressure conditions. As can be seen, variations on the gas flow rate change the intensity and the shape of the current peak. It also modify the time of current peak appearance. For strong flow rates, the current peak exhibits a typical feature of DBDs in a homogenous regime [4]. For low flow rates (below 250 sccm), there is a first peak and then an inflection in the recorded current curve. The difference between low and strong flow rates is clear in discharge electrical characteristics: time-resolved OES is used to examine possible change in plasma chemistry.

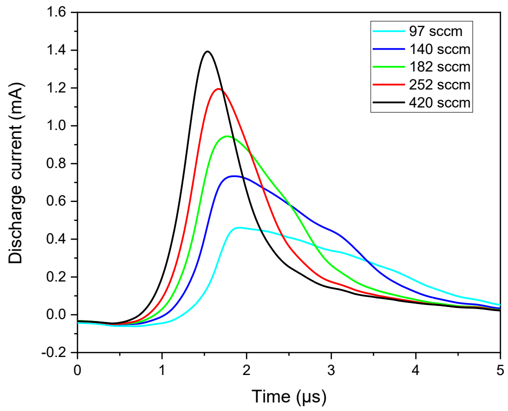

Figure 1. Discharge current as a function of time for different Ar-NH_3 gas flow rates.

In low frequency glow Ar-NH_3 DBDs, main optical emission features in the UV-visible spectrum are the Ar atomic lines (2p-to-1s transition) between 650 and 1150 nm and the molecular emission bands form NH and N_2, between 300 and 400 nm. Since OES measurements are done at the same location for all gas flow rates, knowing the internal surface of the square tube and nature of the gas flow (laminar flow), it becomes possible to link variations in the gas flow rates to variations in the gas residence time. Over the range of experimental conditions investigated, the total flow rate of Ar-NH_3 is varied from 97 sccm to 420 sccm: this corresponds to gas residence times between 50 and 11 ms.

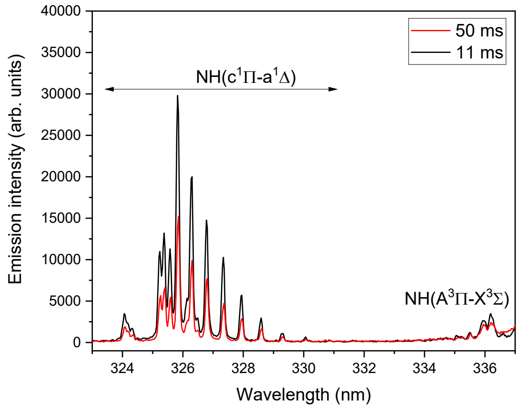

Figure 2. Optical emission spectrum in the UV range of a glow DBD (50 kHz, 2.5 kV) for two residence time of the Penning mixture, 50 ms (in red) and 11 ms (in black)

Figure 2 shows the two NH emission bands for two gas residence times, 50 and 11 ms. The spectra are taken at the time when the emission is most intense. The higher the residence time, the lower the maximum of the two NH emission bands. Focus is made on NH($c^1\Pi$-$a^1\Delta$) (324-330 nm) and NH($A^3\Pi$-$X^3\Sigma$) (336-337 nm) emission bands which can be linked to dissociation and/or by-products of NH_3. These two emission bands can be the result of a direct electron-impact excitation of NH in ground state, because their upper energy level is relatively low (respectively 5.42 and 3.69 eV). However, the NH($A^3\Pi$-$X^3\Sigma$) transition can also result from the dissociative excitation of NH_3 involving a metastable Ar atoms [5]:

$$Ar^* + NH_3 \rightarrow Ar + NH(A^3\Pi) + Hydrogen \qquad (1)$$

$$NH(A^3\Pi) \rightarrow NH(X^3\Sigma) + h\nu \qquad (2)$$

Hence, the NH($A^3\Pi$-$X^3\Sigma$) upper level can be populated by either high-energy electrons or Ar metastable atoms.

The glow DBD examined in this work also emits VUV-UV photons from the de-excitation of a H_2 level. A typical spectrum is shown in Figure 3. The spectrum is taken at the maximum of emission during a LF breakdown. Low emission between 160 and 180 nm is due to O_2 absorption in the 1.2 cm of air before the VUV monochromator.

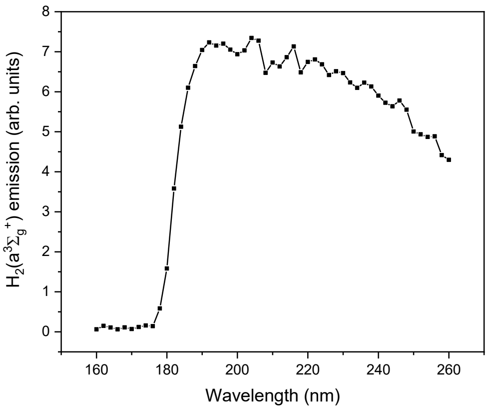

Figure 3. Typical optical emission spectrum in the VUV range of a glow DBD (50 kHz, 2.5 kV) for a gas residence time of 24 ms (in black)

Population of $H_2(a^3\Sigma_g^+)$ states leading to the continuum seen in Figure 3 can involve both electron-impact excitation on $H_2(X^1\Sigma_g^+)$ or energy transfer reactions on $H_2(X^1\Sigma_g^+)$ involving metastable Ar atoms. In an Ar-based plasma at atmospheric pressure, the molecular continuum mostly results from the Penning excitation through the following reaction scheme [6], [7] :

$$Ar^* + H_2(X^1\Sigma_g^+) \rightarrow Ar + H_2(a^3\Sigma_g^+) \qquad (3)$$

$$H_2(a^3\Sigma_g^+) \rightarrow H_2(b^3\Sigma_u^+) + h\nu \qquad (4)$$

This measured emission intensity is presented in Figure 4 at the wavelength of the emission maximum (i.e. 204 nm) as function of the gas residence time in the Ar-NH_3 DBD.

The emission intensities are taken at the maximum of emission during the LF breakdown.

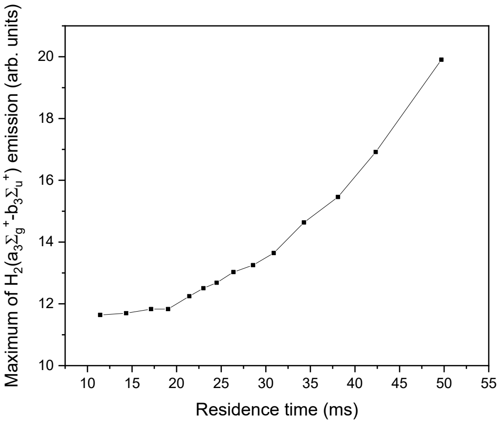

Figure 4. H_2 emission intensity, recorded at 204 nm, as a function of the gas residence time (50 kHz, 2.5 kV).

It can be seen in Figure 4 that the H_2 emission intensity increases with the gas residence time. However, based on Eq. 3, this rise can be linked to an increase of either Ar* or $H_2(X^1\Sigma_g^+)$.

One of the features that could lead to the change in the electrical signature seen in Figure 1 is the NH_3-to-H_2 conversion as a function of the gas residence time. Based on the analysis described above, the H_2-to-NH band ratio could provide interesting information. However, the excitation of $H_2(a^3\Sigma_g^+)$ involves Ar* and $H_2(X^1\Sigma_g^+)$, but the excitation of $NH(A^3\Pi)$ can involve either electrons and $NH(X^3\Sigma)$ on one side, or Ar* and NH_3 on the other side.

A way to examine the dominant excitation pathway is to look at the temporal evolution of the two NH emission bands during a single breakdown. This aspect is shown in Figure 5. From such data, it can be deduce that the 336 nm line is more populated by metastable Ar atoms than the 325 nm emission. The metastable being created by electron impact on ground state Ar atoms and having a lifetime of about 100 ns in such conditions [8], they will accumulate and remain present in the discharge for a short period of time after the current decay. Therefore, at the scale of a low frequency DBD, the NH 336 nm emission should last a little longer than the one populated mostly by direct excitation. This is exactly what can be seen in Figure 5. More specifically, the discharge current peak and the 325 nm emission are similar in their increase and decrease. The 336 nm emission max is shifted by about 50 ns compared to the one of 325 nm or the max of the current peak. Moreover, the decrease of the 336 nm emission is a little bit slower than the 325 nm one. These elements indicate the presence of Ar* in the excitation of $NH(A^3\Pi)$ (Eq. 1).

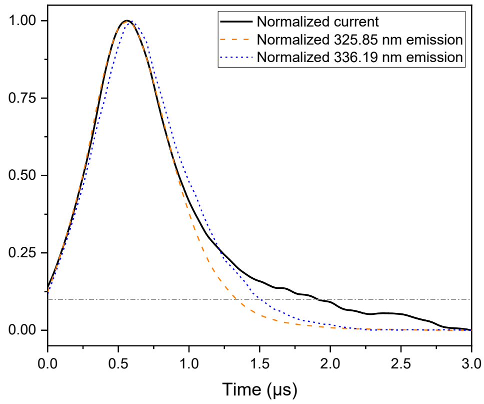

Figure 5. Time-resolved optical emission intensity of NH 325 and 336 nm emission bands (respectively in orange and blue, normalized units), and discharge current (in black, normalized unit) as a function of time during a single breakdown of a low frequency glow DBD for a 11 ms residence time (50 kHz, 2.5 kV).

Placing a threshold on the decay of NH 325 nm (dashed line in Figure 5), one can say that, at this moment, the emission difference between the two NH emissions mostly comes from the excitation of $NH(A^3\Pi)$ by Ar*. Multiplying this difference by the 336 nm emission at this moment, one finds the actual emission of $NH(A^3\Pi)$ due to the dissociative excitation of NH_3 involving a metastable Ar atoms. Based on this value, the measured H_2-to-NH emission band ratio can be assumed proportional to the H_2-to-NH_3 population ratio. This aspect is examined as a function of the gas residence time; the results are shown in in Figure 6.

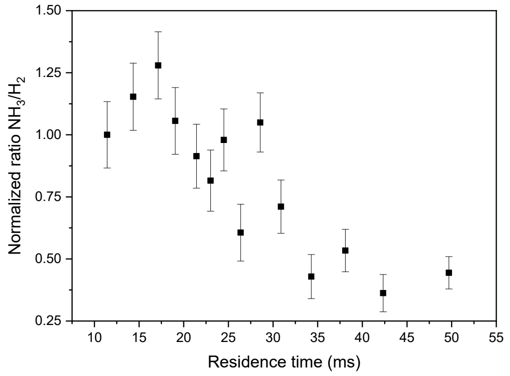

Figure 6. Normalized ratio H_2-to-NH_3 population ratio obtained by optical emission spectroscopy as function of the gas residence time (50 kHz, 2.5 kV).

As expected, by increasing the gas residence time, the quantity of NH_3 decreases and the quantity of H_2 increases. This effect reveals a strong variation in the plasma chemistry of Ar-NH_3 DBDs.

Based in the results presented in Figure 6, the peculiar shape of the discharge current, displayed in Figure 1 at low flow rates, can be better understood. In such conditions, ammonia is significantly consumed and converted to NH and H_2 at the entrance of the discharge. Thus, NH_3 quantity in the discharge is rapidly varying as function of the position. Therefore, the discharge ignites at a given voltage at the discharge entrance. The further away from this point, the lower the amount of ammonia and the higher the voltage required to ignite the plasma. If the discharge ignites at a higher voltage, it ignites later. Since the current is a measure of the total surface area of the electrode, the current peak is longer and weaker than the peak current of high flows; which ignites at the same voltage over the entire electrode. Thus, it is important to keep a high NH_3 quantity all along the discharge to avoid significant variations in the plasma chemistry. Of note, in Figure 6, error bars are quite large because of the uncertainty on the 336 nm emission intensity at the threshold. Further manipulations could allow to obtain a higher light intensity on this emission and thus to decrease the uncertainty associated to this measurement.

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5. References

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