NH$_3$ and HNO$_x$ Formation and Loss in Nitrogen Fixation from Air with Water Vapor by Nonequilibrium Plasma

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ABSTRACT

The current global energy crisis indicated that increasing our insight into non-fossil fuel nitrogen fixation pathways for synthetic fertilizer production is more crucial than ever. Nonequilibrium plasma is a good candidate because it can use N_2 or air as a N source, and water directly as a H source, instead of H_2 or fossil fuel (CH_4). In this work, we investigate NH_3 gas phase formation pathways from humid N_2 and especially humid air up to 2.4 mol% H_2O (100% relative humidity at 20 °C) by optical emission spectroscopy and Fourier-transform infrared spectroscopy. We demonstrate that the nitrogen fixation capacity is increased when water vapor is added, as this enables HNO_2 and NH_3 production in both N_2 and air. However, we identified a significant loss mechanism for NH_3 and HNO_2 that occurs in systems where these species are synthesized simultaneously, i.e., downstream from the plasma, HNO_2 reacts with NH_3 to form NH_4NO_2, which rapidly decomposes into N_2 and H_2O. We also discuss approaches to prevent this loss mechanism, as it reduces the effective nitrogen fixation when not properly addressed, and therefore should be considered in future works aimed at optimizing plasma-based N_2 fixation. In-line removal of HNO_2 or direct solvation in liquid are two proposed strategies to suppress this loss mechanism. Indeed, using liquid H_2O is beneficial for accumulation of the N_2 fixation products. Finally, in humid air we also produce NH_4NO_3 , from the reaction of HNO_3 with NH_3, which is of direct interest for fertilizer application.

INTRODUCTION

Since the invention of synthetic fertilizers, food production increased drastically and enabled mass population expansion.[1] The most important industrial process in the field of nitrogen fixation (NF) (for, among others, synthetic fertilizer production) is the Haber-Bosh (HB) process: a thermo-catalytic conversion of N_2 and H_2 into ammonia.[2] While supporting 50% of the world's

population[3], the HB process depends on fossil fuels for energy and, for the majority of HB chemical plants, as the hydrogen source[4,5] as well. The HB process has been extensively optimized during its 100-year existence, and there is currently no viable alternative or complementary process bringing the same support.[6]

Because of the vital role synthetic fertilizers play and their accompanying high burden on the environment, it is of pivotal importance to research alternative ways for NF to ensure continuous improvement of synthetic fertilizer production. Although these alternative ways cannot fully substitute HB, they can present an appealing auxiliary technology of NF, especially in remote areas with abundant renewable electricity.[7] Moreover, because of the harsh conditions (high temperature and extreme pressure) required for its operation, HB is only economically feasible on large scales[8], resulting in massive centralized production and subsequent costly distribution of the produced NH_3.

Plasma-based NF is therefore an interesting method to consider as an alternative, because it is electricity-based and can use abundant feedstock like air, nitrogen, and water.[9,10] The process is decentralized, can operate on a scale which would fit the very local demand, and is operated at atmospheric pressure, resulting in an overall environmentally and economically friendly local small-scale production, which also eliminates transportation costs.

Plasma is an ionized gas, comprised of electrons, photons, atoms, radicals, ions, and excited species. A variety of plasma sources and feed gases ($N_2/O_2/H_2/H_2O$ combinations) have been reported for plasma-based NF into NO_x[11–15] and NH_3 (in plasma-catalytic[16,17] and plasma-liquid[18] systems). A schematic overview is presented in Figure S1. Most of the reported plasma-based NH_3 production methods rely on H_2, often in the presence of a catalyst.[16,17] Although H_2 can be produced from water via electrolysis, a direct usage of water as a hydrogen source is of interest

for NH_3 production.[10,19] Therefore, studies of NH_3 formation and accumulation in plasma-treated water (PTW)[20–24], sometimes coupled to another technology – a UV source, an ozonator[25–27] and/or an electrochemical cell[28–30] – have been gaining increased interest from both the scientific community and industry. Most of the advances in plasma-based nitrogen fixation are summarized in recent reviews.[10,31]

We have previously shown that H_2O can also be used for the production of NH_3 from mixtures of N_2 and water vapor, and even more interestingly, from air (N_2 and O_2) and water vapor (i.e., humid air), with accumulation of the produced NH_3 in liquid water.[32] However, plasma-based studies that have looked at N_2/H_2O vapor and air/H_2O vapor (i.e., without liquid water) are very scarce.[32,33] Hence, more insight into the gas phase formation of NH_3 with water vapor is needed, not least to understand how NH_3 production can be achieved in both N_2 and air plasma using H_2O as a hydrogen source.

In air/H_2O and N_2/H_2O mixtures, the formation of HNO_x is also of interest. The majority of fertilizers are ammonium salts produced from NH_3 and its oxidation product HNO_3, which is commercially synthesized through the Ostwald process using HB-made NH_3 as feedstock.[10] The direct synthesis of HNO_x alongside NH_3 could therefore result in a more streamlined production process.[34]

This work studies the selectivity of plasma-based NF in air and N_2 discharges at a relative humidity up to 100% at 20 °C (room temperature), i.e. up to 2.4 mol% H_2O. For this, we employed a pulsed plasma jet, which we previously used to study the underlying mechanisms responsible for the record-low energy consumption (EC) value in case of NO_x generation from dry air[35], ultimately yielding a very low overall EC for NH_3 production via plasma-formed NO_x further catalytically reduced into NH_3.[36] More importantly, we also used this plasma jet[32] to

demonstrate that the gaseous H_2O present in the plasma feed gas (and not the liquid H_2O) plays the major role in NF, which was later also observed by Toth et al.[37] Moreover, we showed that both dissolved NH_4^+ and NO_x^- were formed when H_2O vapor was added to the plasma feed gas (N_2 or air). In the present work, we elaborate on this topic, investigating the fundamentals behind the one-step NF process from gaseous N_2/air and H_2O via gas phase diagnostics: Fourier-transform infrared spectroscopy (FTIR) and optical emission spectroscopy (OES), to elucidate the formation mechanisms of the H_2O-based NH_3.

EXPERIMENTAL
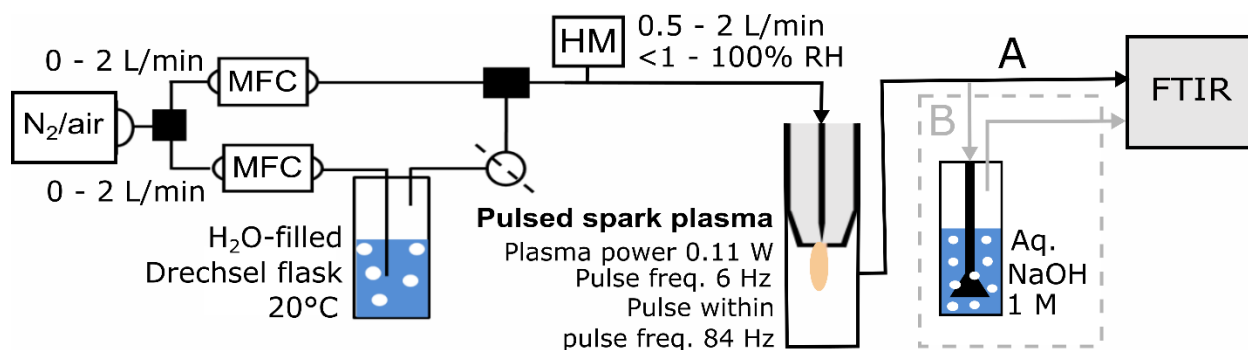
Figure 1. Experimental setup used in this work. Line A shows the setup where the effluent goes straight to the FTIR. Line B shows the setup where the effluent first passes a base washer, indicated in dashed grey. The latter is only used when specified in the text.

Plasma setup. A plasma jet operating in a pulsed spark mode was used, as shown in Figure S2, Supporting information (SI). The peak temperature in one pulse is 1750 ± 150 K, however, the time-averaged temperature is ca. 315 K. Detailed characterization of this device can be found in our previous works.[32,35] Based on the V/I waveforms and discharge imaging, the operational mode of the discharge in both low and high humidity was a low current spark, which is generated in between the pin electrode and the nozzle.[35] The typical duration of the spark is in the range of

700 ns. Due to the nature of the discharge, its characteristics did not change strongly with different humidity levels, as shown elsewhere.[32] The plasma jet was operating either in synthetic air (N_2 + O_2), or pure N_2 (both $\geq$ 99.999%, Air Liquide). The gas flow rate was regulated using two mass flow controllers (MFCs; EL-Flow, Bronkhorst). Partial saturation of the supplied feed gas with H_2O vapor was achieved by splitting the main gas flow and passing its fraction through a water-filled bubbler.[38,39] The resulting gaseous H_2O concentration in the flow was monitored with a humidity meter (Testo 445). The feed gas flow rate was 0.5 or 2 Ls/min (standard liters per minute, henceforth referred to as L/min for simplicity). All tubing in the setup was Swagelok PTFE (diameter ¼ inch). The concentration of H_2O vapor was varied, and will be shown in both molar percentage (<0.1 to 2.4 mol%) and relative humidity at 20 °C (<1 to 100%). We explicitly note that even with no added H_2O vapor, the feed gas contained residual humidity, hence the absence of the zero value humidity. The effluent of the plasma jet was contained within a quartz reservoir (ca. 30 mL volume), the exhaust of which was connected to the FTIR spectrometer, as shown in Figure 1 (length ca. 50 cm).

Downstream gas phase analysis. N-containing stable gaseous products were measured employing FTIR (Matrix-MG2, Bruker, 5 m optical path, using an average of 50 scans, all gas from the setup plasma was directed to the FTIR). Quantitative measurements of NO, NO_2 and N_2O were performed using Bruker's database and Beer's law based on the absorption cross-sections from the HITRAN database[40] The deviation between methods was found to be <3%. The concentration of gaseous NH_3 and HNO_2 were calculated through Beer's law only, using the absorbance cross-section reported by Barney et al..[41] Details on the experimental procedure and data processing can be found in SI, section S3, and Figure S3.

OES analysis of the plasma-produced species. The NO ($A^2\Sigma^+$–$^2\Pi$; 226.94 nm), NH ($A^3\Pi$–$X^3\Sigma$; 336.0 nm), and N_2 ($C^3\Pi$–$B^3\Pi$; Second Positive System; 337 nm) transitions[42] were measured as shown in Figure S4 (section S4 of SI). We performed measurements (i) axially in the plasma (Figure S4a), as well (ii) space-resolved perpendicularly to the plasma effluent (Figure S4b) using (i) a Horiba iHR550 spectrometer with UV 250 nm blazed grating of 2400 g/mm and (ii) a Zolix Omni750 spectrometer with 500 nm blazed grating of 3600 g/mm equipped with a linear fiber optics array slit, respectively. In the axial position, the presented results were corrected for quenching by H_2O, O_2 and N_2, the sensitivity at different wavelengths, and the difference in the electron impact excitation coefficients for the $NO(A^2\Sigma^+)$ and $NH(A^3\Pi)$ states. This means that the intensities of $NO(A^2\Sigma^+)$ and $NH(A^3\Pi)$ bands at different gas mixtures can be compared directly after the performed calculations, i.e. as a function of the humidity. The measured intensities can be correlated to ground state NH and NO densities when assuming that excitation to these states occurs predominantly through electron impact. This approach is based on the following approximations (similar to corona approximation[43]): (1) we do not consider collisional excitations, e.g. $N_2(A^3\Sigma) + NO \rightarrow N_2 + NO(A^2\Sigma)$; (2) the difference in excitation probability is calculated assuming a Maxwell electron energy distribution; (3) we do not consider de-excitation processes through V-V and V-T transfer and charge exchange. We infer that the corrections we made suffice to support the discussion of the obtained results.

The detailed description of the approach, including all computational corrections and normalization based on both experimental data and calculated values can be found in SI, Section S5, Table S1 and S2.

RESULTS AND DISCUSSION

Net production of NH$_3$, NO$_x$ and HNO$_x$ downstream. First, we studied the production of various

stable compounds in the gas phase using FTIR, using the set-up shown in Figure 1, without base

washer, hence following line A. Figure 2a and 2b show the NH$_3$ and HNO$_2$ concentration in N$_2$

at 0.5 L/min and 2 L/min gas flow rate. The results of similar experiments, but with humid air,

are shown in Figure 2c and 2d, where besides NH$_3$ and HNO$_2$ also NO and NO$_2$ were detected.

At all conditions tested, the N$_2$O$_5$, NO$_3$, O$_3$ and HNO$_3$ concentrations were below the limit of

detection. The highest observed N$_2$O concentration did not exceed 2 ppm, and was thus

considered negligible. An overview of the FTIR bands of interest is presented in Figure S3.
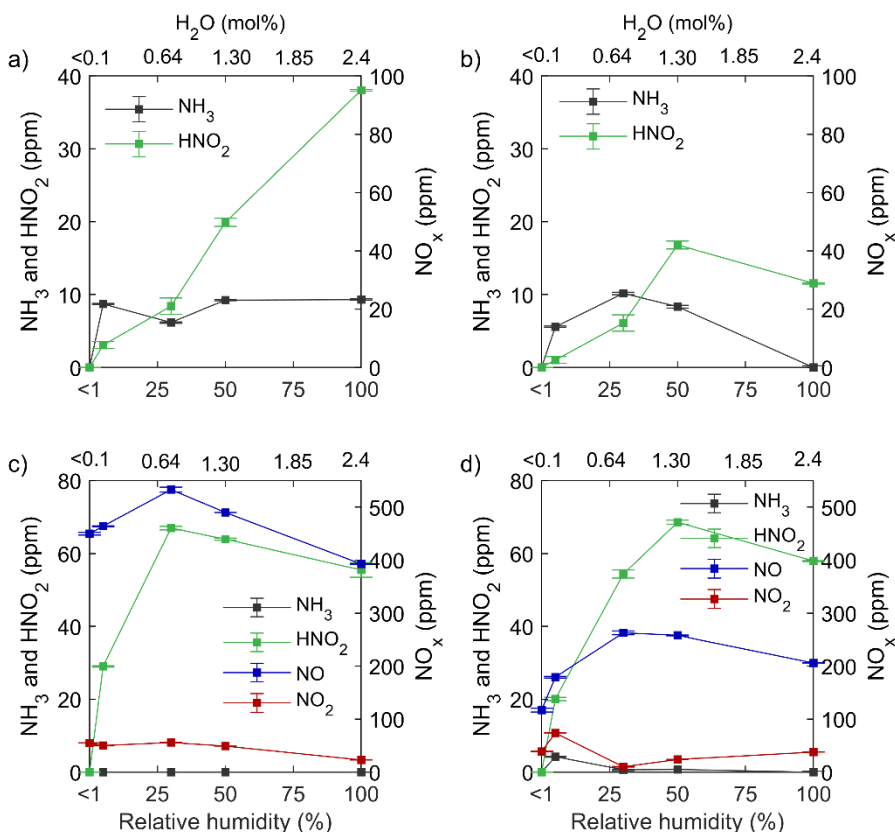
Figure 2. Concentration of NH_3, HNO_2 (left y-axis), and NO_x (right y-axis) in the gas phase as a function of feed gas humidity. (a) N_2, 0.5 L/min; (b) N_2, 2 L/min; (c) air, 0.5 L/min; (d) air, 2 L/min.

In this discussion, we focus on the possible pathways of nitrogen fixation, leading to the production of HNO_2, HNO_3, and NH_3. A discussion on the NO and NO_2 production and their interplay with water can be found in the SI.

As a common trend in both humid N_2 and humid air, when the H_2O content of the feed gas increases, the HNO_2 concentration initially rises, as more H and O become available through H_2O dissociation into H atoms and OH radicals. In N_2 feed gas, since NO is produced predominantly from OH (formed through water dissociation), we observe a continuous increase in HNO_2 concentration with increasing humidity, for 0.5 L/min (Figure 2a), while at 2 L/min, a maximum is reached at 50% relative humidity (Figure 2b). In air, the highest HNO_2 concentration (around 70 ppm) is measured between 25 and 50% relative humidity (Figure 2c and d). Note that the chemistry of the system becomes more complex in humid air compared to humid N_2, rendering a detailed discussion on the mechanisms too speculative. However, a plausible hypothesis why in both N_2 and air, instead of HNO_2 rising until 100% humidity, its concentration decreases at higher H_2O vapor content (i.e., 50–100% for 2 L/min in air and N_2, and 25–100% for 0.5 L/min in air), will be given further down below.

Because H_2O is the sole H source in humid N_2, one could expect the NH_3 concentration to rise with increasing H_2O vapor content as well. However, in the present study the gas phase NH_3 concentration instead stays constant around 10 ppm at humidity above 5% (N_2, 0.5 L/min; Figure 2a) or even starts dropping after reaching a maximum of ca. 10 ppm at 25% humidity (N_2, 2

L/min; Figure 2b). At the same time, in air, despite being H_2O present as an H source, no NH_3 is detected, except for one condition (air, 2 L/min, 5% humidity; Figure 2d). This is counterintuitive, because we previously observed NH_3 accumulation in liquid when the plasma effluent was placed above a water surface, and NH_3 was measured in PTW (as NH_4^+).[32] Additionally, we confirmed in our previous work that most H in the formed NH_3 came from the gaseous H_2O, with only a minor contribution of liquid H_2O to the formation of NH_3. This clearly indicated that NH_3 should be formed in the gas phase of the plasma system, although it is not detected by the downstream FTIR analysis in the present work.

Moreover, HNO_3 (detected in PTW as NO_3^-) was not detected by FTIR in the gas phase under any of the conditions tested. We propose that the reasons are as follows. (i) Gaseous HNO_3 is mainly formed from NO_2 via reaction with $OH^{[36]}$ (see also Table 1 below), however NO_2 is not detected in humid N_2 (Figure 2a and b), and in humid air it is present in low concentrations (much lower than NO) (Figure 2c and d). Furthermore, (ii) we hypothesize the formation of NH_4NO_3 and its precipitation out of the gas phase, as described by Zhu et al.[44] The latter hypothesis was supported by the observed accumulation of white dust during our experiments (see below). Still, we need an in-situ plasma gas phase analysis to elucidate the presence of NH_x species created by the plasma from N_2 and H_2O in both air and nitrogen feed gas, as shown below.

To investigate the near-simultaneous decrease of NH_3 and HNO_2 at high relative humidity (especially for humid N_2 at 2 L/min; Figure 2b), and the absence of detected NH_3 in air when switching from a humid gas-liquid system (as in our previous work[32]) to a pure humid gas system (Figure 2c and d), we studied the chemical species in the plasma and in the plasma afterglow by means of OES (Figure S4a and S4b). OES is a widely used analytical technique for

qualitative and quantitative plasma analysis. It measures the light emission from state transitions in a non-intrusive way, allowing qualitative insight into (short lived) species in the plasma itself and right after the plasma, before potential downstream reactions take place.[45]

OES shows NH and NO are produced in the plasma. First, we analysed the gas composition immediately inside the plasma. This was done by placing the OES spectrometer axially to the plasma jet (see Figure S4a).

The direct OES data provides the intensity of the signals related to the density of excited species. After the made corrections (described above and in the SI, section S5), we can correlate the intensity of the bands of the excited states $NH(A^3\Pi)$ and $NO(A^2\Sigma^+)$ to their ground state density taking into account the approximations behind the corona model applied. This means the resulting corrected data in Figure 3 are representative of the NH and NO ground state concentrations in the plasma. It has been shown that NH is predicative of and correlates with, the concentration of NH_3.[46] In (humid) N_2 the trend of $NO(A^2\Sigma^+)$ intensity follows the gas phase HNO_2 concentration with increasing H_2O content, suggesting NO is directly involved in HNO_2 formation (Figure 3a and 3b).

On the contrary, in (humid) N_2, the NH trend (based on the $NH(A^3\Pi)$ intensity) and the NH_3 trend (measured downstream) show opposite behavior at high humidity (50–100% H_2O content; see Figure 2a and 2b). I.e. inside the plasma the NH generation continues rising throughout the whole humidity range, corresponding to the increase in H_2O (and hence H), as shown in Figure 3a and 3b, while NH_3 decreases or plateaus after 50% humidity. Most importantly, the results with (humid) air not only show the presence of $NH(A^3\Pi)$, but also its increase with increasing H_2O vapor content (Figure 3c and 3d), contrary to the lack of NH_3 in the gas phase downstream

(see Figure 2c and 2d). This clearly demonstrates that the NH_3 precursor NH is produced in the plasma, both in humid N_2 and air. This discrepancy in the NH behavior compared to NH_3 suggests that NH_3 is "lost" after the plasma, before the downstream FTIR analysis. In order to obtain insights in the aforementioned pathway of NH_3 decomposition, we used spatially resolved emission spectroscopy, perpendicularly to the plasma effluent (Figure S4b). For these conditions we also measured $N_2(C^3\Pi–B^3\Pi)$ (see below), and found a correlation between NO and the excited state of N_2. Indeed, next to ground state and vibrationally excited N_2, electronically excited N_2 also plays a role in the main formation reactions of NO, i.e. the Zeldovich mechanism (RS1 and RS2, in the SI).[35]
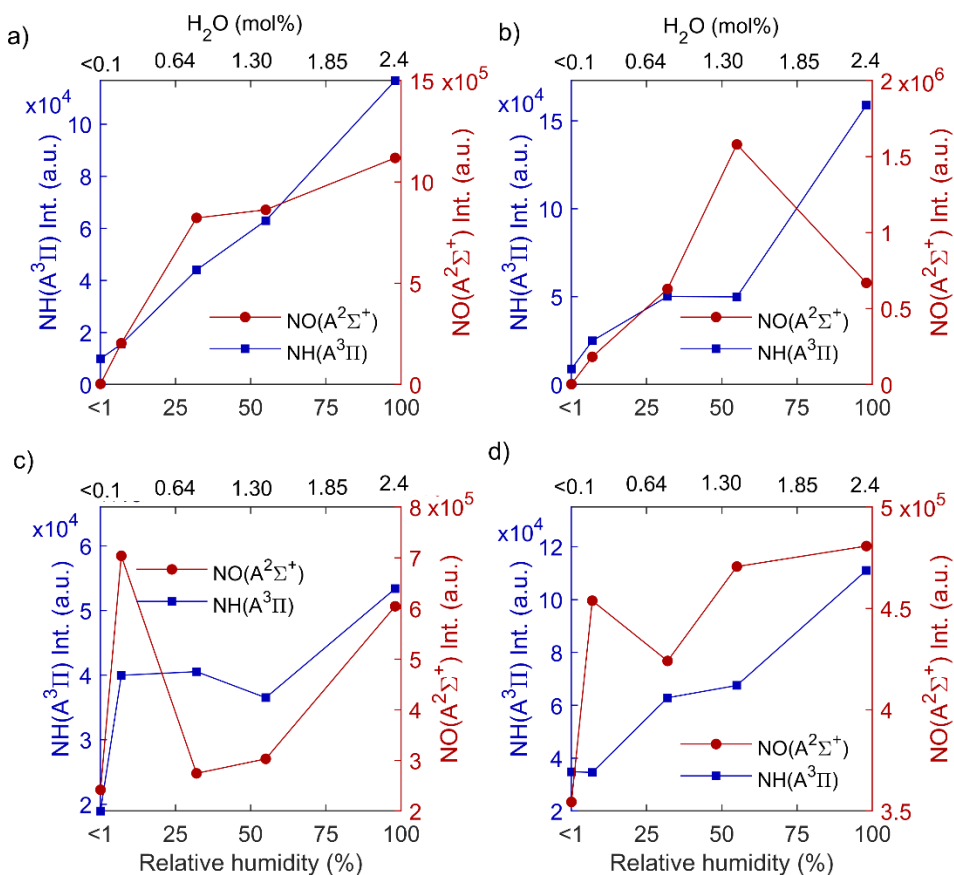
Figure 3. NH(A$^3\Pi$) (left y-axis)and NO(A$^2\Sigma^+$) (right y-axis) intensities in the plasma as a function of feed gas humidity. (a) N$_2$, 0.5 L/min; (b) N$_2$, 2 L/min; (c) air, 0.5 L/min; (d) air, 2 L/min.

NH presence in the plasma afterglow. In the afterglow, the following state transitions were observed: NH(A$^3\Pi$–X$^3\Sigma$), N$_2$(C$^3\Pi$–B$^3\Pi$) and NO(B$^2\Pi$–X$^2\Pi$). The NO(A$^2\Sigma^+$–X$^2\Pi$) transition was below the limit of detection in the afterglow under the conditions studied, however, the NO(B$^2\Pi$–X$^2\Pi$) transition is visible in the 338–340 nm region for some conditions. Figure 4 shows typical emission spectra (334–340 nm) along the plasma jet stream measured at the distance from 1 to 10 mm from the jet's outlet (or nozzle), for 5% relative humidity in N$_2$ and air, at 2 L/min. Spectra for all other conditions (N$_2$ and air, 0.5 and 2 L/min, from <1 to100% relative humidity) are found in Figure S5.
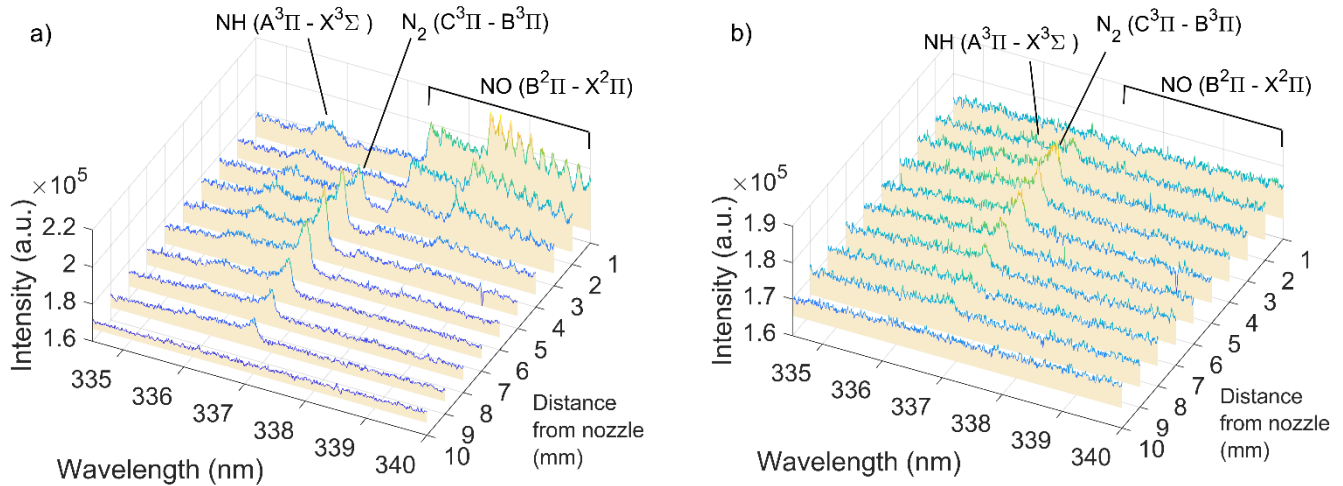
Figure 4. Emission spectra (334–340 nm) as a function of distance from the jet nozzle (1–10 mm), for 5% relative humidity at 2 L/min, in N$_2$ (a) and air (b).

It is worth noting that N$_2$(C$^3\Pi$–B$^3\Pi$) was also observed in the axial OES. However, there its

presence is non-informative. In contrast, the space-resolved perpendicular OES allowed us to draw conclusions on the relationship between various chemical species present in the plasma afterglow.

While no direct correlation between $NO(B^2\Pi–X^2\Pi)$ and either of the $NH(A^3\Pi)$ and $N_2(C^3\Pi)$ was found, the obtained data allowed us to draw conclusions on the relationship between $NH(A^3\Pi)$ and $N_2(C^3\Pi)$. At all conditions, $NH(A^3\Pi)$ correlates strongly with the presence of $N_2(C^3\Pi)$ in the plasma and in the afterglow. Indeed, next to vibrationally excited N_2, electronically excited N_2 also plays a role in the splitting of N_2, which is a necessary step in NH formation.[35]

Interestingly, at low humidity (5–30%) in N_2, another excited state, $N_2(B^2\Pi)$, is formed through high energy electrons, and is effectively quenched at higher H_2O concentrations and at higher O_2 fractions.[47] This is the reason why the $NO(B^2\Pi)$ emission is visible only in N_2 gas, and only at low humidity (Figure 4a; see also Figure S5k, q and to a lesser extent l and r). $NH(A^3\Pi)$ is observed in N_2 even when only trace amounts of H_2O vapor are present (see Figure S5k and S4p in SI), due to the relatively low excitation energy needed for NH ground state excitation (3.68 eV)[48], and because there is only a small amount of strong quenchers present (i.e. H_2O) for $NH(A^3\Pi)$[49,50] in the feed gas.

As discussed above, no NH_3 was detected in the gas phase downstream when humid air was used as feed gas. At the same time, we have measured NH_3 in liquid when the plasma was placed above liquid water[32] and we observe by OES the formation of $NH(A^3\Pi)$, an indicator for NH_3, when humid air is used, both in the plasma and in the afterglow.

NH₃ and HNOₓ loss through salt formation and decomposition. To explain this discrepancy, we considered that NH_3 can form salts with HNO_x and looked at the most commonly reported

pathways for the formation and decomposition of NH_4NO_x (summarized in Table 1, R1-R8).[51–53] It is known from selective catalytic reduction process (SCR) that NO_x and HNO_x can react with NH_3, which facilitates their conversion into N_2 and H_2O via NH_4NO_2 and NH_4NO_3 intermediates. Unlike in SCR, in plasma synthesis, the formation of NH_4NO_2 is undesirable as it decomposes back to N_2 and H_2O at room temperature and atmospheric pressure.[54] On the other hand, NH_4NO_3 is more stable and requires higher temperatures to undergo decomposition (R7).[52,55,56] The formation of NH_4NO_x has been observed in plasma systems as well, e.g. in a dielectric barrier discharge (DBD) plasmas which focus on NH_3 oxidation.[57,58]

In our experimental setup, the residence time between the plasma and the FTIR (0.07 and 0.3 s for 2 and 0.5 L/min, respectively) is sufficient to allow complete conversion of NH_3 and HNO_2 into NH_4NO_2 (assuming reaction R3). Indeed, the timescale for loss of NH_3 (drop in concentration from 50 ppm to 0.1 ppm) would be around 0.1 s, making NH_4NO_2 formation a plausible pathway in this system.

Table 1. Relevant reactions, and corresponding reaction rate coefficients and relevant temperature ranges, for the formation and decomposition of NH_4NO_x.

Reaction	Rate coefficient [a] /Equilibrium constant (R9) [b]	Temperature range		Ref
$NO + OH + M \rightarrow HNO_2 + M$	7.52×10^{-31} $(T/300)^{-2.4}$	200–400 K	R1	59
$NO_2 + OH + M \rightarrow HNO_3 + M$	1.63×10^{-30} $(T/300)^{-2.9}$	300–600 K	R2	60
$HNO_2 + NH_3 \rightarrow [NH_4NO_2]$	3.65×10^{-18}	298 K	R3	61
$HNO_2 + NH_4NO_3 \rightarrow [NH_4NO_2] + HNO_3$	n/a		R4	53

$[NH_4NO_2] \rightarrow N_2 + 2H_2O$	n/a (unstable)	<400 K	R5	[54]
$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$	$2.46 \times 10^{10} \times$ (118.87 – 24084/T – 6.025×ln(T))	265–305 K	R6	[62]
$NH_4NO_3 \rightarrow N_2O + 2H_2O$ [c]	$10^{6.7} \times e^{-86/RT}, 10^{14} \times e^{-207/RT}$	350–600 K	R7	[63]
$NH_4NO_3 + NO \rightarrow NO_2 + NH_4NO_2$	n/a		R8	[53,64]

M is any neutral molecule and T is the gas temperature

[a] Unit: $cm^3/(molecules \cdot s)$ for two-body reactions, and $cm^6/(molecules^2 \cdot s)$ for three-body reactions.

[b] Unit: $molecules^2/cm^6$

[c] In the temperature range 530 - 560 K, 98% of the irreversible decomposition of NH_4NO_3 occurs via this reaction.[65] However, in NO rich conditions R8 is more favourable.[53]

Therefore, we hypothesize that downstream from the plasma in our system HNO_2 reacts with NH_3 to form NH_4NO_2, which rapidly decomposes into N_2 and H_2O (R3-R5).[55,66] We note that NH_4NO_2 can also be formed through HNO_3 as an intermediate (R4). However, we assume this pathway to be negligible in our experiments because we observe HNO_3 neither in the gas nor in the liquid.

Another plausible explanation is the precipitation of NH_4NO_3, which has also been described in SCR systems and as a direct product in plasma systems.[52,55,56] However, in the case of N_2 as feed gas, formation of NH_4NO_3 is unlikely: this would require HNO_3 being present, but we detected HNO_3 neither in the gas phase (this work) nor in PTW in our previous work.[32] Therefore, we infer that while in humid air plasma the loss of NH_3 is possible through NH_4NO_3 (R6, R7 and R8) and NH_4NO_2 (R3, R4, R5 and R8), in N_2 plasma the loss of NH_3 at higher humidity levels, as seen in Figure 2a and 2b, occurs almost solely through NH_4NO_2.

To confirm our hypothesis about NH_4NO_x, we performed an in-line removal of HNO_2 (and possibly HNO_3) immediately after plasma by adding a Drechsel flask with 1M aqueous solution

of NaOH (see Figure 1, following line B, i.e. including the base washer). This basic medium completely dissolves gaseous HNO_x, while hindering the solvation of gaseous NH_3 which thus passes further downstream, as was shown in the case of N_2 with H_2O vapour.[23] Figure 5 shows the effect of HNO_x removal on the FTIR spectra, reflected in the NH_3 concentration measured in the gas phase downstream from plasma. When an alkaline medium is added to trap HNO_2, the concentration of NH_3 in humid air goes from non-detectable (cf. also Figure 2c and d) to clearly detectable (Figure 5). Specifically, at 2 L/min air, 100% RH, we measured NH_3 concentration of ca. 50 ppm in the gas phase. This fully supports our above hypothesis.

Thus, we demonstrate for the first time that NF from air with H_2O vapor proceeds via a pathway towards NH_3 as well as NO_x/HNO_x, but this can be overlooked because of the product loss downstream due to side reactions leading to NH_3 decomposition.
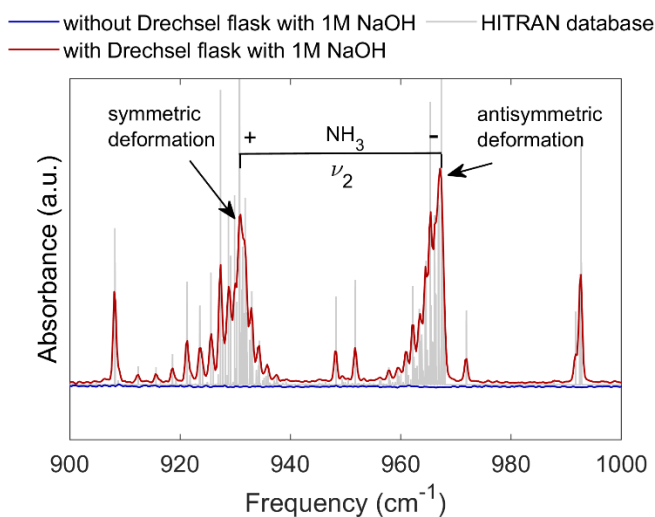
Figure 5. FTIR spectra of the NH_3 ν_2 deformation region, with and without HNO_x removal by NaOH, at 100% relative humidity in air, 2 L/min. The symmetric and antisymmetric deformations of NH_3 are shown, together with the simulated NH_3 spectrum in this range as obtained from the HITRAN database.[67]

These data are consistent with the drop in HNO_2 and NH_3 concentrations at a H_2O content above 30% relative humidity (Figure 2). Once HNO_2 and NH_3 are produced simultaneously, NH_4NO_2 starts being formed and further decomposes, thus effectively decreasing the net HNO_2 and NH_3 production. In air, the concentrations of the generated HNO_x are certainly higher than in N_2, due to the presence of O_2 and associated oxidative pathways. At the same time, in air the concentration of NH_3 is likely lower due to the larger contribution of competing reactions with the excited N_2 molecules (i.e., oxidative versus reductive NF). As a result, some (but not all) NH_3 and some HNO_x are likely lost due to the NH_4NO_x formation when N_2 is the feed gas, while virtually all NH_3 is lost when using air.

This effect appears to be slightly different at 0.5 L/min in N_2 (Figure 2a). Even though the NH_3 concentration plateaus instead of rises upon increasing humidity, both HNO_2 and NH_3 do not drop (as is the case with other high humidity conditions, Figures 2b and 2d), and HNO_2 even shows a rising trend until 100% humidity. While the specific reasons for this are unclear at this point, we propose that the adverse effect of NH_4NO_x formation is still present, because otherwise the continuous rise of NH_3 concentrations should be observable. This question presents an important point for further research aimed at decreasing this loss mechanism, next to the use of an in-line HNO_2 removal.

However, as mentioned above, NH_4NO_2 is not the only salt formed from NH_3 and HNO_x. In our experiments, we observed the build-up of a fine white powder in the quartz tube used during the OES experiments, Qualitative analysis of the powder via the indophenol blue reaction (described elsewhere[27,68]) demonstrated that the cation of the salt was indeed NH_4^+.[24,47] Due to the limited availability of analytical equipment, the anion could not be identified, but a negative Griess reagent test[69] excluded the presence of NO_2^-. This is in agreement with NH_4NO_2 not being a

stable product at atmospheric pressure and room temperature[54] (see Table 1). Therefore, we conclude that the anion was likely NO_3^-, in agreement with Zhu et al.[44], who observed NH_4NO_3 dust formation after operating plasma which contained both NH_3 and NO_x. We note, however, that the amount of solid formed after weeks of our experiments (at different flow rates and humidity values) was in the range of mg. This is due to the (likely) very low amount of HNO_3 formed in our plasma.[70] Indeed, although low concentrations of HNO_3 would be expected in our experiments because substantial amounts of NO_2 are produced in the gas phase with air plasma, no HNO_3 was detected. Hence, it is reasonable to conclude that all formed HNO_3 reacted with NH_3 to form NH_4NO_3. Interestingly, when liquid H_2O was used to accumulate the NF products, both NO_3^- and NH_4^+ were detected in PTW with air plasma. In case of a close liquid surface, NH_4NO_3 did not precipitate out of the gas phase due to the short flight time to the liquid surface. Liquid water prevents decomposition via dissolution; the coordination of ions with water molecules in solution stabilizes the ions and inhibits decomposition reactions.

Furthermore, a semi-quantitative assessment of the relative loss pathways in this case was performed, with humid air. We performed the experiment with 2 L/min of air, 100% RH, for 3 h, during which we observed precipitate deposition on the tubing. After this, a gravimetric analysis of the precipitate was performed by washing the precipitate off the walls of the tubing. After evaporation of water, the mass of the accumulated precipitate was found to be below 5 mg. As shown above, by introducing the alkaline washer, 50 ppm of NH_3 was "recovered" under these conditions (we note once again that the alkaline washer is not selective, and removes HNO_x rather than only HNO_2 or only HNO_3). This amounts to ca. 74 nmol/s of NH_3. From the stoichiometry of NH_4NO_3 formation, we conclude that after 3 h the amount of precipitate would constitute 64 mg if all of it was NH_4NO_3 – which is not the case. Thus, the relative contribution

of the NH_4NO_3 pathway to NH_3 loss does not exceed 10%. Therefore, even in the humid air plasma, most of NH_3 is lost via the generation and subsequent decomposition of NH_4NO_2. Although performance optimization is not the focus of this work, we also assessed the energy consumption (EC) and the production rate (PR) of NF in our experiments. The numerical EC values and the calculation method are presented in the supporting information in Table S5 and S6. The relative improvement in a hypothetical scenario when NH_3 and HNO_2/HNO_3 are not lost in our experiments was evaluated. Let us consider example conditions of humid air plasma operated at 2 L/min, 100% RH, i.e. the same conditions at which the experiment with the HNO_x-removing washer was performed. Here, we detect 50 ppm of NH_3, which means also 50 ppm HNO_x was lost. The overall concentration of NF products without accounting for the NH_4NO_x loss is ca. 300 ppm (see Figure 2d), which becomes 400 ppm when NH_4NO_x is not lost. Therefore, the relative decrease in EC, and the relative increase in PR, when the product loss is avoided amounts to ca. 30%. Using liquid water as a reservoir to accumulate the nitrogen fixation products can aid in this. Taken together, these data clearly suggest that using liquid H_2O in proximity to the plasma zone is beneficial: it increases the total net accumulation of the NF products, because it reduces or even eliminates the loss of NH_4NO_x.

CONCLUSIONS

We studied the pathways of nitrogen fixation in humid N_2 and humid air plasma using optical emission spectroscopy and Fourier-transform infrared spectroscopy. We revealed that the increased NH emission, as well as NH ground state density, strongly correlates with the water vapor content in both N_2 and air plasmas, indicating that the reduction nitrogen fixation pathway (towards NH_3 formation) takes place in both gas mixtures.

We show for the first time that NH_3 is produced in air plasma in non-negligible quantities (in the same order of magnitude as HNO_2, and only an order of magnitude lower than NO and NO_2 combined). However, in both air and N_2, this nitrogen fixation pathway is strongly affected by the presence of HNO_2 and HNO_3.

In humid air, the formation of both NH_4NO_3 and NH_4NO_2 likely occurs. Although both of these can decrease the process efficiency downstream, part of NH_3 remains in fixated form as precipitated NH_4NO_3. In contrast, in humid N_2 we ascribe the loss pathway exclusively to NH_4NO_2, which is unstable and decomposes to N_2 and H_2O, decreasing the overall nitrogen fixation efficiency.

In summary, our work shows that (1) the selectivity of nitrogen fixation in air and N_2 plasmas can be controlled by changing the humidity of the feed gas, (2) NH_3 production can be achieved in both N_2 and air plasma using H_2O as a hydrogen source, and (3) the adverse effects of NH_4NO_2 formation hinder the net production, and therefore the overall efficiency, of the plasma-based nitrogen fixation process. The latter means that, under conditions where HNO_2 and NH_3 are produced simultaneously, it is important to suppress the reverse process (via decomposition of NH_4NO_2). This can be performed through an in-line removal of HNO_2 from the gas mixture, or by using plasma-treated water to accumulate all nitrogen fixated products simultaneously without losses.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge at https://pubs.ac.org/.... (PDF), and includes additional details on the experimental setups of optical analyses, calculational methodology for OES and FTIR, and further experimental data.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ˣThese authors contributed equally.

ABBREVIATIONS

HB, Haber-Bosch process; NF, nitrogen fixation; PTW, plasma-treated water; UV, ultra violet; EC, energy consumption; FTIR, Fourier transform infrared spectroscopy; OES, optical emission spectroscopy; MFC, mass flow controller; Ls, standard liter.

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For Table of Contents Use Only
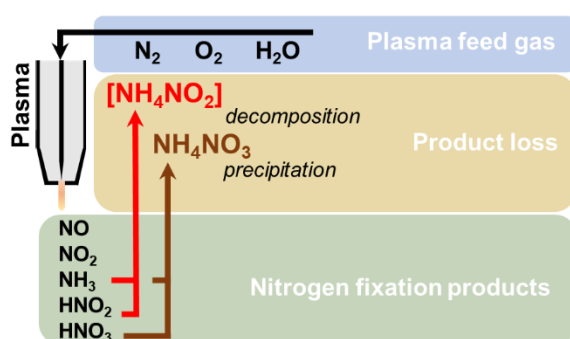
SYNOPSIS We demonstrate in-situ production of NH_3 in nitrogen fixation from N_2 and air with H_2O vapor, and show that the efficiency of the process can be increased by avoiding the consequent loss of NH_3 via formation of NH_4NO_2.

Supporting Information

NH$_3$ and HNO$_\mathrm{x}$ Formation and Loss in Nitrogen Fixation from Air with Water Vapor by Nonequilibrium Plasma

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Contents

S1. Schematic of the plasma device

Figure S1. Various pathways for plasma-based nitrogen fixation with a focus on the different possible hydrogen sources. The current industrial process is shown as a reference in blue. Each full line represents a possible pathway towards basic fertilizer chemicals.

S2. Schematic of the plasma device
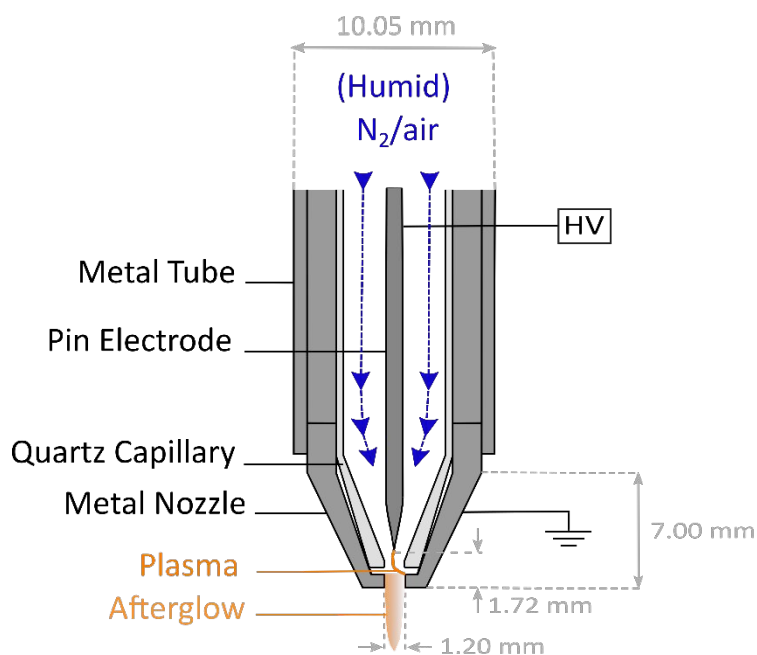
Figure S2. Schematic of the plasma device. HV stands for high voltage electrode.

S3. FTIR analysis

Absorbance spectra measured by Fourier transform infrared spectroscopy revealed the presence of several vibrational transitions which correspond to NO, NO_2, N_2O, NH_3, and HNO_2 species. The Bruker system (with the OPUS gas analysis software) was factory-calibrated for NO, NO_2, N_2O, O_3 and N_2O_5. The remaining peaks were identified using the HITRAN database.[1] Their concentrations were determined by measuring a reference signal from the gas mixture with a known concentration of the species of interest and *via* Beer's law as follows[2]:

$$n_j = \frac{ln\left(I(v)/I_0(v)\right)}{\sigma_j(v) \cdot L} \times \left(\frac{10^{12}}{n}\right) \tag{S1}$$

where $ln\left(I(v)/I_0(v)\right)$ is the measured absorbance ($A(v)$) as a function of wavenumber (v), σ_j (v) is the absorption cross-section of species j as a function of v [in cm^2 molecule^{-1}], and L is the length of the absorbance pathway [in cm]. The last term in the brackets performs the unit conversion from (cm^{-3}) to (ppm), where n is the gas density at 323 Kelvin (the temperature in the gas cell). This method is commonly used in gas analysis using FTIR.[3–5] Though for NO, NO, NO_2 and N_2O the concentration was determined through both Beer's law and the Bruker system, all concentrations reported are determined using Beer's law, for consistency.

Figure S1 shows the theoretical absorbance peaks for NO, NO_2, N_2O, NH_3, HNO_3, HNO_2 and O_3. Species present in detectable quantities were NO, NO_2, NH_3 and HNO_2, though not at all conditions. The concentration of N_2O was <2 ppm for all conditions measured. HNO_3 was not detected at any of the examined conditions, as well as O_3 due to the relatively high gas temperature of the afterglow.
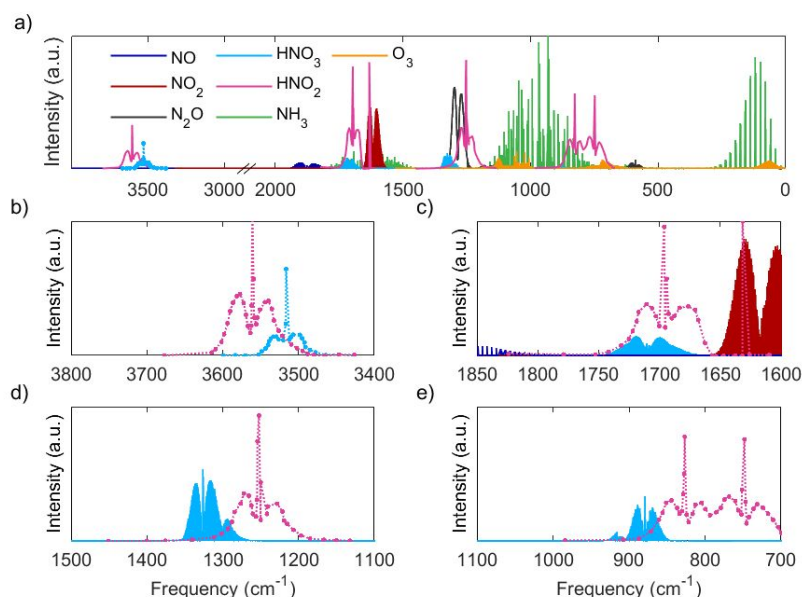
Figure S3. (a) Overview of absorption bands from NO, NO$_2$, N$_2$O, HNO$_3$, HNO$_2$, NH$_3$ and O$_3$. (b) HNO$_2$ and HNO$_3$ bands in the 3400 – 3800 cm^{-1} region. (c) HNO$_2$, HNO$_3$, NO and NO$_2$ bands in the 1550 – 1850 cm^{-1} region. (d) HNO$_2$ and HNO$_3$ bands in the 1100 - 1500 cm^{-1} region. (e) HNO$_2$ and HNO$_3$ bands in the 700 - 1100 cm^{-1} region. All simulated spectra have been taken from the HITRAN database[1], except for HNO$_2$ and the HNO$_3$ region 3700 – 3800 cm^{-1} annotated with dashed lines, which were digitized from Pipa et al.[6] based on literature values.[7,8]

S4. Experimental setups of OES
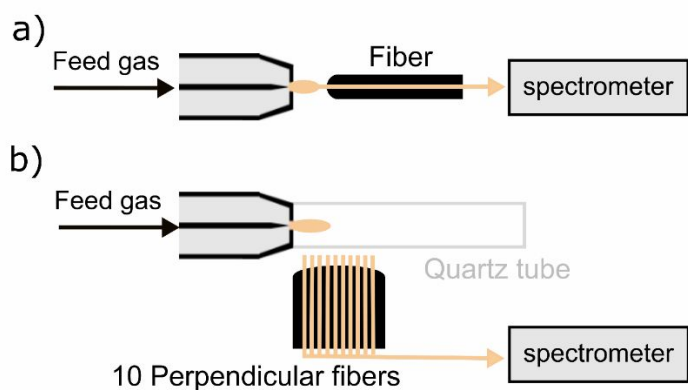
Figure S4. Basic gas analysis experimental setup as explained in the main text. (a) OES setup axial to the jet. (b) OES setup perpendicular to the afterglow using 10 fibers for spatially resolved measurements (1-10 mm from the nozzle).

S5. Optical emission spectroscopy

NH(A$^3\Pi$–X$^3\Sigma$) can be detected at 336.00 nm; there are no major interferences in this region.

The main pathway for production of NH(A³Π–X³Σ) is through NH$_3$. It is commonly accepted that NH(A³Π–X³Σ) is a good indication of the NH$_3$ density.[9]

$$NH_3 + e \rightarrow NH(A^3\Pi) + H_2 + e \qquad k(\sigma)^{[10]} \qquad\qquad (RS1)$$

The NO (A²Σ⁺–B²Π) transition was detected at 226.94 nm. The NO (B²Π–X²Π) transition (around 340 nm[11]) was only observed in the afterglow. Both NO(A²Σ⁺) and NO(B²Π) states are formed mainly through:

$$e + NO \rightarrow e + NO(A^2\Sigma^+) \qquad k(\sigma)^{[12]} \qquad\qquad (RS2)$$

$$e + NO \rightarrow e + NO(B^2\Pi) \qquad k(\sigma)^{[12]} \qquad\qquad (RS3)$$
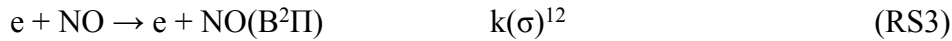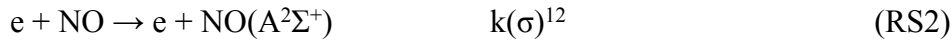
In order to correlate intensities of excited species measured in OES to ground state densities and to compare different bands with each other, a number of corrections and approximations have to be considered as follows:

(1) Quenching of excited states is taken into account.
(2) The measured intensities are corrected for the spectrometer sensitivity and fibre optics transparency.
(3) The signals are corrected to take into account the difference in excitation probabilities associated with the different transitions used. This means the emission of the excited states can be linked to the emission of the ground state.

These corrections have been made under the assumptions of the corona model approximation (explained in sections S5.1-S5.3 below).

S5.1. Correction for quenching by H$_2$O, O$_2$ and N$_2$

Quenching reduces the fraction of the state that can be observed through photon emission[13] and collisional quenching reduces the effective branching ratio of a spontaneous transition $i \rightarrow k$. Following Hartinger et al.[14], the quenching of the excited species can be expressed as shown in eq. S1. Here q represents the fraction of the excited species that is present after quenching.

$$q = \frac{A}{A+Q}, \text{ where } Q = \Sigma n_i v_{ri} \sigma_I \qquad\qquad (S2)$$

A Einstein transition coefficient (s^{-1})
Q effective quenching rate (s^{-1})
n_i number density of the quenching partner i (cm^{-3})
v_{ri} relative velocity (cm/s)
σ_I cross section (cm^2)

In case quenching coefficients instead of cross sections are given, Q is expressed as follows:

$$Q = \Sigma n_i k_{iq} \qquad\qquad (S3)$$

k_{iq} quenching coefficient (cm^3/s)

The Einstein transition coefficient denotes the total spontaneous emission rate of the upper level, which is equal to its reciprocal lifetime. For NO($A^2\Sigma^+$–$^2\Pi$) A is taken from LIFBASE[15]. For NH($A^3\Pi$–$X^3\Sigma$) A is taken from Zhou et al.[16] The values are reported in the summary Table S1. Q is a sum over all possible quenchers, taking into account their density.

The relative speed of the quencher to the quenched molecule is calculated as follows:

$$v_{rel} = \sqrt{\frac{8kT}{\pi\mu}} \qquad\qquad (S4)$$

with $\mu = \dfrac{1}{\frac{1}{m_1} + \frac{1}{m_2}} = \dfrac{m_1 m_2}{m_1 + m_2}$ in (g/particle) $\qquad\qquad (S5)$

Meaning $m_i = \dfrac{1}{M_i \cdot N_A}$ $\qquad\qquad (S6)$

With:

$k = 1.380649 \times 10^{-16} cm^2 g/(s^2 K)$, for v_{rel} expressed in cm/s.

This also means that

$$k_{iq} = \sigma_i v_{rel} \qquad\qquad (S7)$$

For both the quenching coefficients and cross-section there are a wide range of values found in literature. In this work the Q values from three sources were calculated and their average was used as the quenching coefficient. The three sets of constants are shown in Table S2.

With q known, the signal corrected for quenching is calculated using eq. 10:

$$I_{measured} = I_{orginal} \cdot q \qquad\qquad (S8)$$

q	fraction of the signal that is visible after quenching
$I_{measured}$	measured signal
$I_{original}$	the signal without quenching

Table S1. Einstein transitions coefficients of NH($A^3\Pi$–$X^3\Sigma$) and NO($A^2\Sigma^+$)

Einstein transition coefficient A (1/s)		
NO($A^2\Sigma^+$–$^2\Pi$)	9.8×10^5	17
NH($^3\Pi$–$^3\Sigma$)	1.39×10^6	16

Table S2. The cross sections and rate coefficients for NH($A^3\Pi$) and NO($A^2\Sigma^+$) quenching by N_2, O_2 and H_2O as collisional quenchers.

Quencher	Cross section (NH($A^3\Pi$)) (cm^2)		Rate coefficient (NO($A^2\Sigma^+$)) (cm^3/s)		
	Set A	Set B	Set C	Set D	Set E

N_2	0.1×10^{-16}	[13]	0.0061×10^{-16}	[18]	0.00047×10^{-10}	[19]	0.00065×10^{-10}	[20]	0.00074×10^{-10}	[19]
O_2	1.5×10^{-16}	[13]	4.3×10^{-16}	[18]	1.47×10^{-10}	[19]	1.46×10^{-10}	[20]	1.59×10^{-10}	[21]
H_2O	9.8×10^{-16}	[13]	9.8×10^{-16}	[18]	7.71×10^{-10}	[19]	7.8×10^{-10}	[20]	7.58×10^{-10}	[21]

S5.2 Correction for sensitivity

The difference in light collection at different wavelengths was measured and used to correct the NH($A^3\Pi$ –$X^3\Sigma$) and NO($A^2\Sigma^+$–$^2\Pi$) band intensities. As a light source, a Hamamatsu D2 model L7293 lamp was used with a C9598 power supply.

S5.3 Correction for excitation probability

The correction for the excitation probability can be applied under the approximation that the systems behaves as assumed in the corona model. The corona approximation is a simplified approach to population densities in nonequilibrium plasmas. It assumes an equilibrium where transition upwards for ionization and excitation occurs solely through electron impact, and the transitions downwards only occurs through spontaneous emission and radiative decay. As we are working at atmospheric pressure and our averaged temperature is low, this means we do not take into account collisional recombination, 3-body recombination, step-wise excitation, charge exchange, and V-V and V-T processes.[22]

Direct electron impact excitation requires electrons with an energy above 5.48 eV and 3.68 eV, for NO($A^2\Sigma^+$–$^2\Pi$) and NH($A^3\Pi$–$X^3\Sigma$),[23] respectively. The corresponding excitation probability will be different by the following factor (eq. 11):

$$\frac{P(NO)}{P(NH)} = \frac{n_{e>5.48\,eV}}{n_{e>3.68\,eV}} \times \frac{\exp\left(\frac{EE_{NO}}{k_b \cdot T_e}\right)}{\exp\left(\frac{EE_{NH}}{k_b \cdot T_e}\right)} = 0.17 \times \frac{n_{e>5.48\,eV}}{n_{e>3.68\,eV}} \tag{S9}$$

P probability of electron impact excitation
n_e electron density
T_e electron temperature
k_b Boltzmann constant

The ratio of the density of electrons with the required energy for the excitation to NO($A^2\Sigma^+$) and NH($A^3\Pi$) can be presented by the fraction of electrons assuming a Maxwell-Boltzmann energy distribution, which results in an excitation factor of 0.0331 for NO($A^2\Sigma^+$) excitation compared to NH($A^3\Pi$). It has to be noted that the considered corona-model corrected for quenching processes is valid for low ionization degree plasmas with only electron impact excitation mechanisms. Additional excitation processes can lead to overestimation of the excited states density in the corona model. However, a model including a complete set of population processes would require a collisional-radiative model which is not yet available in literature for mixtures such as used in our work.

S6. NO_x formation in (humid) N_2 and air

This is a discussion based on the NO and NO_2 trends presented in Figure 2 of the manuscript. Describing the detailed reaction mechanisms for HNO_x, NO, NO_2 and NH_3, as well as their interplay, requires dedicated computational studies based on a chemical kinetics model, which can take into account large reaction sets, while incorporating the plasma parameters (e.g., power density) as input. We did this for a much simpler chemical system consisting only of dry air[24], where we discussed how reverse reactions of the Zeldovich mechanism can be suppressed and the vibrational nonequilibrium can be promoted through the use of pulsed power and resulting pulsed temperature. A complete computational model with added H_2O would be much more complex, and was outside the scope of the present work. However, based Based on our general insights obtained from our other models, data from literature, and our present experimental data, we can hypothesize the following mechanisms.

In brief, in humid N_2 the dominating mechanism for NO and NO_2 formation is the extended Zeldovich mechanism (see RS1 in Table S3), as discussed by Gromov et al.[25], because H_2O is the sole oxygen source. However, the concentrations of NO and NO_2 were below 1 ppm for the whole range of used H_2O content (<1-100% relative humidity)), likely because all NO_x reacted further to form HNO_2, as seen in Figure 2a and 2b.

On the other hand, in humid air where O_2 is readily available, the NO_x concentration is not only dramatically higher than in humid N_2 (where NO_x concentration was <1 ppm), but is up to 4 times higher than the HNO_2 concentration (e.g., 69 ppm HNO_2, 254 ppm NO_x at 50% relative humidity and 2 L/min; Figure 2d). In this scenario, NO_x formation is guided by both the traditional non-thermal (RS2 and RS3) and the extended Zeldovich mechanisms (RS1) shown in Table S3.

Table S3. (Extended) Zeldovich reactions, their corresponding reaction rate coefficients and relevant temperature ranges.

Reaction	Rate coefficients [a]	Temperature range		Ref
$N + OH \rightarrow NO + H$	4.7×10^{-17}	300–2500 K	RS1	26
$O_2 + N \rightarrow NO + O$	$4.47 \times 10^{-12} \times e^{-27188/RT}$	298–5000 K	RS2	26
$N_2 + O \rightarrow NO + N$	$3.01 \times 10^{-10} \times e^{-318000/RT}$	1400–4000 K	RS3	26
[a] Unit: $cm^3/(molecules \cdot s)$ for two-body reactions, and $cm^6/(molecules^2 \cdot s)$ for three-body reactions. T is the gas temperature.				

S7. OES spectra recorded perpendicular to the plasma effluent

Table S4. Overview of the waterfall plot conditions and their respective Figure numbers.

Gas	Air									
Flow rate (Slm)	0.5					2				
Relative humidity at 20°C (%)	<1	5	30	50	100	<1	5	30	50	100
Figure S4.	a	b	c	d	e	f	g	h	i	j
Gas	N_2									
Flow rate (Slm)	0.5					2				

Relative humidity at 20°C (%)	<1	5	30	50	100	<1	5	30	50	100
Figure S4.	**k**	**l**	**m**	**n**	**o**	**p**	**q**	**r**	**s**	**t**

Figure S5. Emission spectra (334–340 nm) as a function of the distance from the jet nozzle (1–10 mm). The full list of the experimental conditions (Figures S5a – S5t) is shown in Table S3 above.

b

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

×10⁵

Wavelength (nm)

Distance from nozzle (mm)

c

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

×10⁵

Wavelength (nm)

Distance from nozzle (mm)

d

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

$\times 10^5$

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

1
2
3
4
5
6
7
8
9
10

Distance from nozzle (mm)

e

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

$\times 10^5$

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

1
2
3
4
5
6
7
8
9
10

Distance from nozzle (mm)

s13

f

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.)

×10^5

Wavelength (nm)

Distance from nozzle (mm)

g

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.)

×10^5

Wavelength (nm)

Distance from nozzle (mm)

h

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.) ×10^5

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

Distance from nozzle (mm)

1
2
3
4
5
6
7
8
9
10

i

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.) ×10^5

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

Distance from nozzle (mm)

1
2
3
4
5
6
7
8
9
10

j

NH (A³Π - X³Σ)
N₂ (C³Π - B³Π)
NO (B²Π - X²Π)

k

NH (A³Π - X³Σ)
N₂ (C³Π - B³Π)
NO (B²Π - X²Π)

l

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.)

×10^5

Wavelength (nm)

Distance from nozzle (mm)

m

NH (A$^3\Pi$ - X$^3\Sigma$)

N$_2$ (C$^3\Pi$ - B$^3\Pi$)

NO (B$^2\Pi$ - X$^2\Pi$)

Intensity (a.u.)

×10^5

Wavelength (nm)

Distance from nozzle (mm)

n

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

$\times 10^5$

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

1
2
3
4
5
6
7
8
9
10

Distance
from nozzle (mm)

o

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

$\times 10^5$

1.9
1.8
1.7
1.6

335
336
337
338
339
340

Wavelength (nm)

1
2
3
4
5
6
7
8
9
10

Distance
from nozzle (mm)

s18

p

NH (A³Π - X³Σ)

N₂ (C³Π - B³Π)

NO (B²Π - X²Π)

q

NH (A³Π - X³Σ)

N₂ (C³Π - B³Π)

NO (B²Π - X²Π)

s19

r

NH ($A^3\Pi$ - $X^3\Sigma$)

N$_2$ ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

×10^5

2.2

2

1.8

1.6

Wavelength (nm)

335 336 337 338 339 340

Distance
from nozzle (mm)

1 2 3 4 5 6 7 8 9 10

s

NH ($A^3\Pi$ - $X^3\Sigma$)

N$_2$ ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

Intensity (a.u.)

×10^5

2.2

2

1.8

1.6

Wavelength (nm)

335 336 337 338 339 340

Distance
from nozzle (mm)

1 2 3 4 5 6 7 8 9 10

s20

t

NH ($A^3\Pi$ - $X^3\Sigma$)

N_2 ($C^3\Pi$ - $B^3\Pi$)

NO ($B^2\Pi$ - $X^2\Pi$)

$\times 10^5$

Intensity (a.u.)

Wavelength (nm)

Distance from nozzle (mm)

S8. *Energy consumption and production rate*

Using the plasma power (P) and the total (H)NO_x concentration, the EC was calculated according to eq. 12. The EC is expressed in MJ/(mol N), where mol N is the amount of nitrogen fixed. The power was close to constant for all conditions, as discussed in detail elsewhere[24,27], hence in the first approximation the same plug power (1.04 W) was used for all conditions.

$$EC\left(\frac{MJ}{mol}N\right)$$

$$= \frac{P(W)}{mol\,of\,(H)NO_x\,produced\,per\,second\left(\frac{mol}{s}\right)} \times \frac{1}{10^6\left(\frac{J}{MJ}\right)} ==$$

$$\frac{P(W) \times 10^6 \times 60\left(\frac{s}{min}\right) \times 22.4\left(\frac{L}{mol}\right)}{(C_{HNO2} + C_{NO2} + C_{NO} + C_{NH3})\,(ppm) \times Flowrate\left(\frac{L}{min}\right) \times 10^6\left(\frac{J}{MJ}\right)} \quad \text{(S10)}$$
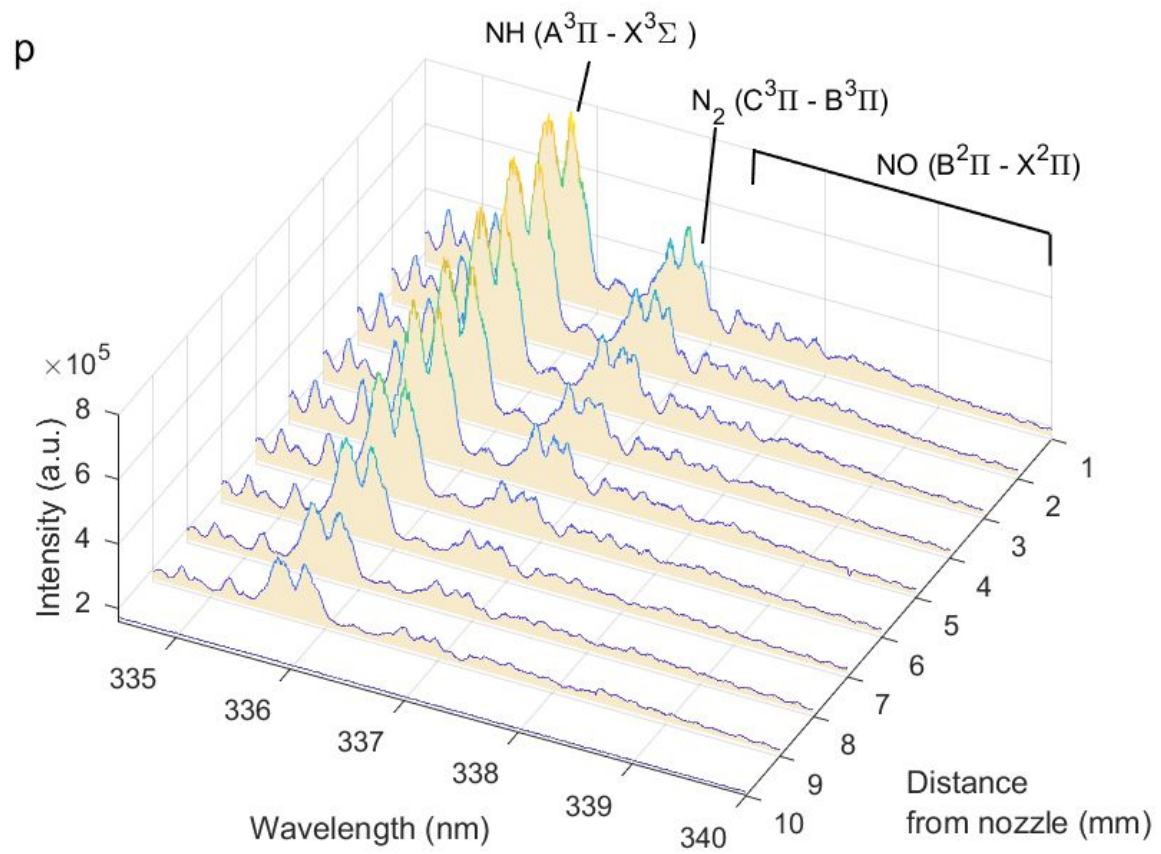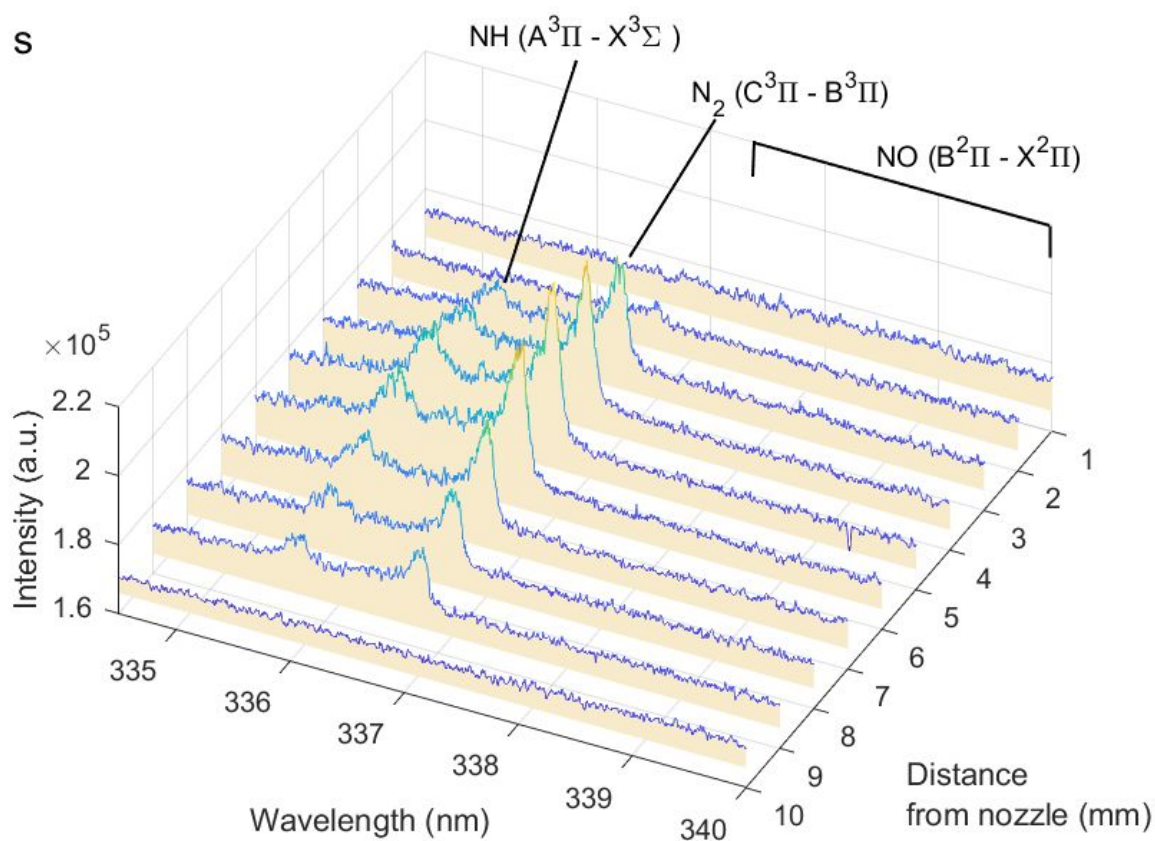
The detailed methodology of energy consumption calculations is given in our previous work.[24] It has to be emphasized here that for clarity of the results we only report the total energy consumption, which can be drastically improved by optimization of the power supply system. As shown in our previous results, both experimentally and numerically, the plasma power

which is used to support the sustaining of the discharge, can be a factor of magnitude lower than the total power. The engineering challenge is to design a power system where power efficiency is optimized which is however out of the scope of our current research. Note that the values of the plasma EC look much better, i.e., with values of 0.42 MJ/(mol N fixed)[24], but they don't account for the power supply efficiency, and for real application, the total EC should be considered.

As seen from the data, even the lowest EC we observed is still ca. 4 times higher than the EC of Haber-Bosch, which is 0.48 MJ/(mol N). Nonetheless, plasma has the advantage of being able to use renewable electricity, because of its fast switch on/off capacity, and is therefore promising for distributed fertilizer production. We infer that plasma processes should be used as an auxiliary technology, rather than substituting the current industrial state-of-the-art entirely.

Table S5. Average energy consumption (EC) of nitrogen fixation.

Flow rate (L/min)	Relative Humidity (%)	EC (MJ/(mol N fixed)	
		Air	N_2
0.5	<0.1	5.54	-
	5	5.40	238.01
	30	5.03	192.28
	50	4.79	78.25
	100	6.12	59.22
2	<0.1	4.45	-
	5	3.37	106.03
	30	2.93	43.13
	50	2.18	22.03
	100	2.70	60.76

The production rate (PR) of the various products (x), and the conversion of N_2 in our system was calculated as shown in eq. 13 and 14:

$$PR_x\left(\frac{mg}{h}\right) == \frac{C_x\ (\text{ppm}) \times Flow\ rate\left(\frac{L}{min}\right) \times 60\left(\frac{min}{h}\right)}{22.4\left(\frac{L}{mol}\right) \times 10^3} \times M_x\left(\frac{g}{mol}\right)\ (S11)$$

$$N_2\ conversion\ (\%) = \frac{(C_{HNO2} + C_{NO2} + C_{NO} + C_{NH3})\ (\text{ppm})}{N_2\ fraction\ in\ the\ feed\ gas\ (\text{ppm}) \times 2} \times 100\%\ (S12)$$

Table S6. Average production rate (PR) of the products of nitrogen fixation, and the conversion of N_2.

Flow Rate (L/min)	Relative Humidity (%)	PR (mg/h)								N_2 conversion (%)	
		Air				N_2				Air	N_2
		NO	NO_2	NH_3	HNO_2	NO	NO_2	NH_3	HNO_2		
0.5	<0.1	18	3.4	-	-	-	-	-	-	0.032	-
	5	17	2.7	-	1.8	-	-	0.20	0.19	0.032	0.00059
	30	18	2.7	-	4.2	-	-	0.14	0.53	0.035	0.00073
	50	19	2.9	-	4.0	-	-	0.21	1.3	0.037	0.0018
	100	15	1.7	-	3.5	-	-	0.21	2.39	0.029	0.0024
2	<0.1	19	9.9	-	0.0	-	-	0.00	0.00	0.010	-
	5	23	11	-	5.1	-	-	0.51	0.26	0.013	0.00033
	30	23	11	-	14	-	-	0.92	1.5	0.015	0.00081
	50	37	6.1	-	17	-	-	0.76	4.2	0.020	0.0016
	100	29	5.3	-	15	-	-	0.00	2.9	0.016	0.00058

We note that the EC and PR values shown are not compensated for the losses due to the NH_4NO_2 decomposition and NH_4NO_3 precipitation because the experiments with the alkaline washer were not performed for every condition used.

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