Supporting Information

Unraveling Non-Equilibrium Generation of Atomic Nitrogen and Hydrogen in Plasma Aided Ammonia Synthesis

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1. **Voltage and current measurements**

The voltage was measured using a high voltage probe (Tektronix P6015A) with a digital oscilloscope (Tektronix TDS 2012B). The current was measured by a current monitor (Pearson 6585). Figure S1 shows the example voltage and current measurements within a period at 20 kHz and 18 kV.

![Voltage and Current Measurements](image)

Figure S1. Voltage and current measurements in a 0.9 N₂/0.1H₂ AC plasma discharge at 20 kHz and 18 kV. The pressure is 100 Torr.

2. **TALIF calibration**

As mentioned in the main text, the TALIF calibration for inferring absolute number density of N and H was performed using Krypton (Kr) fs-TALIF measurements, because H, N and Kr shared similar excitation and fluorescence wavelengths with minor changes only. The absolute density of the target species (i.e., N or H atoms) denoted as \( N_i \) is determined by comparing against the known number density of the calibration species Kr (denoted as \( N_C \)) as follows:

\[
N_i = N_C \frac{\eta T_C}{\eta T_i} \frac{\sigma_{2 \rightarrow 3C}}{\sigma_{2 \rightarrow 3i}} \left( \frac{\int_0^\infty P^2(t) dt}{\int_0^\infty P^2(t) dt} \right) \frac{\int_0^\infty I^2(t) dt}{\int_0^\infty I^2(t) dt} \frac{g(\delta v)_C}{g(\delta v)_i} \frac{S_{Di}}{S_{DC}}
\]

where \( \eta \) and \( T \) are the quantum efficiency of the camera and the transmission of the signal collection optics at the fluorescence wavelength, \( \int_0^\infty P^2(t) dt \) is proportional to the square of the used pulse energy, \( v_0 \) is the central wavelength of the excitation laser, \( \frac{\sigma_{2 \rightarrow 3i}}{\sigma_{2 \rightarrow 3C}} \) is the two-photon absorption cross section ratio of the
target species against the calibration species (0.62 and 0.67 for $\sigma_{K_r}^{(2)}$ and $\sigma_{K_r}^{(2)}$, respectively obtained from Ref 2), $g(\delta v)$ is the normalized two-photon absorption line profile, $S_{Di}$ and $S_{DC}$ are the measured fluorescence signals, and subscript C and $i$ represent the calibration and target species, respectively. $a_{2\rightarrow3} = \frac{A_{2\rightarrow3}}{A_{2}+Q}$ is the fluorescence quantum yield where $A_{2\rightarrow3}$ is the Einstein coefficient taken from Ref 3, 4. In $a_{2\rightarrow3}$, $A_{2}$ and $Q$ are the spontaneous emission rate and collisional quenching rate, respectively, and $A_{2} + Q = \frac{1}{\tau} + \sum_{q} k_{q} n_{q}$ where $\tau$ is the natural lifetime of the species (34.1 ns, 17.6 ns and 29.6 ns for Kr, H and N, respectively) \(^3,5,6\), $k_{q}$ is quenching coefficient of the collisional partner with $q$ taken to be the major species N$_2$ and H$_2$ obtained from Ref 2, 4, and $n_{q}$ is the number density of the collisional partner calculated based on the ideal gas law with the approximate mole fractions, i.e., 0.1 and 0.9 for H$_2$ and N$_2$, at 100 Torr and the temperatures measured by Rayleigh scattering.

3. Rayleigh scattering for gas temperature measurements

The gas temperature was measured in-situ using Rayleigh scattering. In Rayleigh scattering, the signal is proportional to the total number density of molecules in plasma. In this work, the Rayleigh scattering was first used to measure the total number density of molecules, which was then combined with the ideal gas law to obtain the temperature. Note that here Rayleigh scattering can be directly used for measuring total number density of molecules, because the concentrations of major species (i.e., N$_2$ and H$_2$) in the N$_2$/H$_2$ plasma are stable (i.e., only a small portion of N$_2$ and H$_2$ was converted into NH$_3$), and the combined cross section of Rayleigh scattering keeps constant. Figure S2 shows the experimental setup for Rayleigh scattering. A Nd:YAG laser (Quantel Q-Smart 850) produced laser pulses with a wavelength of 532 nm, a pulse duration of 6 ns, a pulse energy of 45 mJ, and a shot-to-shot variation of pulse energy within ± 5%. The laser pulses were focused by a plano-convex lens of focal length 1 m into the central region of the N$_2$/H$_2$ plasma reactor. The Rayleigh scattering signals from the plasma were captured by an ICCD camera (Princeton Instruments PIMAX-4 1024i) with a gate time of 80 ns. The camera was equipped with a lens (Nikon AF-S Nikkor 50mm f/1.8) and a bandpass filter of bandwidth 1 nm and central wavelength 532 nm to block the interferences at other wavelengths. The synchronization between the laser and the camera was achieved through a delay generator (SRS DG645). 50 shots of Rayleigh scattering signals were averaged to minimize the laser pulse shot-to-shot variation. To determine the gas temperature, the Rayleigh signals were calibrated using the reference Rayleigh signals at room temperature and 100 Torr.
Figure S2. Schematic of the in-situ Rayleigh scattering measurements. The system focused Nd:YAG laser pulses (532 nm wavelength, 6 ns pulse duration, and 45 mJ pulse energy) into the central line of the plasma. The Rayleigh signals were captured by a camera, which were then combined with ideal gas law to obtain temperature. L: plano-convex lens, $f = 1000$ mm; F: bandpass filter, 532 nm ± 0.5 nm.

4. Numerical method and kinetic model

The numerical modeling for the time evolution of species densities in a plasma discharge is calculated by an integrated zero-dimensional (0-D) hybrid ZDPlasKin-CHEMKIN model\textsuperscript{7,8}. The model incorporates the plasma kinetics solver ZDPlasKin\textsuperscript{9} and the gas phase kinetics solver CHEMKIN II\textsuperscript{10} by a time-slitting scheme\textsuperscript{11}. The electron impact reaction rate constants and transport coefficients are solved by the Boltzmann equation solver BOLSIG+\textsuperscript{12} which is incorporated in ZDPlasKin. The global equations (S2) and (S3) of the first-order splitting algorithm are shown as follows,

$$\frac{\rho_{i}^{n+1} - \rho_{i}^{n}}{\Delta t} = \omega_{i}^{\text{plasma}} + \omega_{i}^{\text{gas}}$$

(S2)

$$\frac{T_{n+1} - T_{n}}{\Delta t} = \Delta T_{\text{plasma}} + \Delta T_{\text{gas}}$$

(S3)

where $\rho_{i}^{n+1}$ and $\rho_{i}^{n}$ are the densities of species $i$ at time steps $n+1$ and $n$, respectively, $t$ the time, and $\omega_{i}^{\text{plasma}}$ and $\omega_{i}^{\text{gas}}$ the reaction rates of species $i$ in plasma kinetic mechanism solved by ZDPlasKin and gas phase mechanism solved by CHEMKIN II. For the temperature calculation, $T_{n+1}$ and $T_{n}$ are the temperatures at time steps $n+1$ and $n$. $\Delta T_{\text{plasma}}$ and $\Delta T_{\text{gas}}$ are the temperature rise contributed by the plasma and gas phase mechanisms, respectively.

Integration of equation (S2) and (S3) is carried out the following time-splitting mechanism (S4) - (S7),
\[
\frac{(\rho_i^{n+1} - \rho_i^*)}{\Delta t} = \omega_i^{\text{plasma}} \quad (S4)
\]

\[
\frac{(\rho_i^* - \rho_i^n)}{\Delta t} = \omega_i^{\text{gas}} \quad (S5)
\]

\[
\frac{(T_n^{n+1} - T^*)}{\Delta t} = \Delta T_{\text{plasma}} \quad (S6)
\]

\[
\frac{(T^* - T^n)}{\Delta t} = \Delta T_{\text{gas}} \quad (S7)
\]

where \(\rho_i^*\) is the intermediate density and \(T^*\) is the intermediate temperature between the calculation of ZDPlasKin and CHEMKIN II.

A \(\text{N}_2/\text{H}_2\) plasma chemistry for \(\text{NH}_3\) synthesis\(^{13-16}\) is developed and validated in this work. This kinetic model comprises two parts, a plasma kinetic sub-mechanism involving electrons, ions and excited species calculated by ZDPlasKin, and a gas phase sub-mechanism of ground states calculated by CHEMKIN II. The kinetic model consists of 50 species, 494 reactions in the plasma kinetic mechanism and 51 reactions in the gas phase mechanism. The species included in the model are listed in Table S1. The plasma kinetic sub-mechanism incorporates the reactions of electron impact vibrational excitation, electronic excitation, dissociation, ionization and attachment, as well as the energy exchange and quenching of vibrationally and electronically excited species, charge exchange, electron attachment, ion-ion and electron-ion recombination. The cross-section data of electron impact reactions are primarily obtained from the Phelps database\(^{17}\). Note that the dissociation cross sections of \(\text{N}_2\) are taken from Cosby\(^{18}\) which performs a better prediction of \(\text{N}\) number density. The cross sections of \(\text{H}_2\) ionization are obtained from the IST-Lisbon database\(^{19}\) with more detailed data at different electron energies. For the cross sections not available in Phelps database, the dissociative ionization of \(\text{N}_2\) and the attachment of \(\text{H}_2\) are from Itikawa database\(^{20}\), and the ionization of \(\text{H}\) and \(\text{N}\) are from Morgan database\(^{21}\). The gas phase sub-mechanism involving the reactions of ground states is from Thorsen et al.\(^{22}\). In the sub-mechanisms, the cross sections and rate constants of elementary reactions are obtained from the experimental measurements and theoretical/quantum calculations both with validations, which are annotated in the Supporting Mechanisms.

The rate constants of chemical abstraction reactions involving vibrationally excited species are calculated by on Fridman-Macheret \(\alpha\)-model\(^{23}\). The coefficient of vibrational excitation energy in overcoming the activation barrier \(\alpha\) is calculated by

\[
\alpha \approx \frac{E^f}{(E^f + E^r)}
\]

(S8)
where $E_f^a$ is the forward reaction activation energy, and $E_r^a$ is the reverse reaction activation energy. Then the rate constant of an elementary reaction involving an excited molecule with vibrational energy $E_v$ can be accelerated by decreasing the activation energy by $E_a - \alpha E_v$.

**Table S1. Species included in the N\textsubscript{2}/H\textsubscript{2} plasma chemistry.**

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Radicals</th>
<th>Excited species</th>
<th>Charged species</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}, N\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}H\textsubscript{4}</td>
<td>H, N, NH, NH\textsubscript{2}</td>
<td>H\textsubscript{2}(v=1) - H\textsubscript{2}(v=3),</td>
<td>H\textsuperscript{+}, H\textsubscript{2}\textsuperscript{+}, H\textsubscript{3}\textsuperscript{+},</td>
</tr>
<tr>
<td>NNH, tHNNH, cHNNH, H\textsubscript{2}NN, N\textsubscript{2}H\textsubscript{3}</td>
<td>N\textsubscript{2}(v=1) - N\textsubscript{2}(v=8),</td>
<td>N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=0) - N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=7),</td>
<td>N\textsuperscript{+}, N\textsubscript{2}\textsuperscript{+}, N\textsubscript{3}\textsuperscript{+}, N\textsubscript{4}\textsuperscript{+},</td>
</tr>
<tr>
<td>(N\textsubscript{2}(A) is the summation of N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=0) - N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=1) ; N\textsubscript{2}(B) is the summation of N\textsubscript{2}(B\textsuperscript{3}\Pi\textsubscript{g}), N\textsubscript{2}(W\textsuperscript{3}\Delta\textsubscript{u}) and N\textsubscript{2}(B\textsuperscript{3}\Sigma\textsubscript{u}); N\textsubscript{2}(a\textsuperscript{\prime}) is the summation of N\textsubscript{2}(a\textsuperscript{\prime}\textsuperscript{1}\Pi\textsubscript{g}), N\textsubscript{2}(a\textsuperscript{1}\Pi\textsubscript{g} and N\textsubscript{2}(w\textsuperscript{1}\Delta\textsubscript{u}); N\textsubscript{2}(C) is the summation of N\textsubscript{2}(C\textsuperscript{3}\Pi\textsubscript{u}), N\textsubscript{2}(E\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{+}) and N\textsubscript{2}(a\textsuperscript{\prime\prime}\Sigma\textsuperscript{g}+)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**5. Model validation**

To validate the N\textsubscript{2}/H\textsubscript{2} plasma chemistry for the predictions of N and H number densities, the comparison with the experiment results by Yang et al.\textsuperscript{13} is conducted. The time-solved number densities of metastable N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=0)/N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+},v=1) and temperature were measured by tunable diode laser absorption spectroscopy (TDLAS) in N\textsubscript{2} and N\textsubscript{2}/H\textsubscript{2} plasmas during a repetitively-pulsed nanosecond discharge (NSD). The ground state N and H atoms were measured by two-photon absorption laser-induced fluorescence (TALIF).

In our numerical modeling for NSD, the voltage across the discharge gap $U_{\text{gap}}$ is calculated by

$$
\frac{dU_{\text{gap}}(t)}{dt} = (1 + \frac{2l_d}{\varepsilon_d L})^{-1} \left( \frac{dU_{\text{app}}(t)}{dt} - \frac{2I_d}{\varepsilon_0 \varepsilon_d} j(t) \right)
$$

(S9)

where $l_d$ is the dielectric layer thickness, $\varepsilon_d$ the relative dielectric constant, $L$ the gap distance, $U_{\text{app}}$ the voltage applied to the electrodes, $\varepsilon_0$ the vacuum permittivity, and $j$ the discharge current density. The parameters used in the model are the same as the experiments of Yang et al.\textsuperscript{13}.

The electric field strength in the discharge gap $E_{\text{gap}}$ is calculated by

$$
E_{\text{gap}}(t) = \frac{U_{\text{gap}}(t)}{L}
$$

(S10)
Figure S3 shows the applied voltage as well as the calculated voltage and the reduced electric field strength $E_{\text{gap}}/N$ (where $N$ is the gas number density) across the discharge gap in a single nanosecond discharge pulse. The calculation is conducted in a N$_2$ plasma discharge at 150 Torr. Figure S3 shows that the electric field in the discharge gap increases with the applied voltage. When the breakdown occurs, the electric field quickly drops. This inhibits the energy coupling to the discharge channel due to the sheath shielding.

Figure S3. Applied voltage and calculated voltage and reduced electric field strength across the discharge gap.

In our calculation, the experimentally measured temperature is used as input for accurately considering the Joule heating and heat loss in the plasma discharge. Figure S4 shows the measured temperature from Yang et al.$^{13}$ and the fitted temperature used in the model during a 150-pulse burst with a pulse repetition rate of 100 kHz in a N$_2$ plasma discharge.

Figure S5 shows the comparison of N number density between the TALIF measurement from Yang et al.$^{13}$ and the model prediction. The results show that the present numerical methods and kinetic model can well predict the N number density measured by TALIF. Figure S5 shows that the N concentration increases faster in the first 10 pulses. This is due to the contribution by metastable N$_2$($A^3\Sigma^+_u,v$) molecules via N$_2$($A^3\Sigma^+_u,v$) + N$_2$($A^3\Sigma^+_u,v$) → N$_2$ + N + N as studied by E R Jans et al.$^{24}$ besides the direct dissociation of N$_2$ by electrons via $e + N_2 \rightarrow e + N + N(2D)$. Figure S6 shows that time evolutions of number densities of the first two vibrational levels N$_2(A^3\Sigma^+_u,v=0)$ and N$_2(A^3\Sigma^+_u,v=1)$. The results show the present model can agree well with the experimental measurement. The number densities of $N_2(A^3\Sigma^+_u,v=0)$ and $N_2(A^3\Sigma^+_u,v=1)$ increase in the first 10 pulses which are consistent with the N increment. In this stage,
$N_2(A^3\Sigma_u^+, v=1)$ contributes to N production significantly. However, with N accumulation, the concentration of $N_2(A^3\Sigma_u^+, v=0)$ and $N_2(A^3\Sigma_u^+, v=1)$ decrease rapidly after 10 pulses via $N_2(A^3\Sigma_u^+, v) + N \rightarrow N_2 + N$. Therefore, the N production rate decreases and is primarily contributed by the direct electron impact dissociation of $N_2$.

Figure S4. Measured temperature from Yang et al.\textsuperscript{13} and fitted temperature used in the present model during a 150-pulse burst with a pulse repetition rate of 100 kHz in a $N_2$ plasma discharge at 150 Torr.

Figure S5. N number density comparison between the TALIF measurement from Yang et al.\textsuperscript{13} and the model prediction in the present work during a 150-pulse burst with a pulse repetition rate of 100 kHz in a $N_2$ plasma discharge at 150 Torr.
Figure S6. Time evolutions of (a) $N_2(A^3\Sigma_u^+,v=0)$ and (b) $N_2(A^3\Sigma_u^+,v=1)$ number densities of the TDLAS measurement from Yang et al. and the model prediction in the present work during a 150-pulse burst with a pulse repetition rate of 100 kHz in a N$_2$ plasma discharge at 150 Torr.

In addition to the validation on the pure N$_2$ plasma discharge, we also extended the model validation to a H$_2$/N$_2$ plasma with mole fractions of 0.01 and 0.99, respectively. The discharge parameters for the H$_2$/N$_2$ plasma remain the same as those for the N$_2$ mixture, and the corresponding results are summarized in Figures S7 and S8. Figures S7 and S8 show the comparison between the experiment and model prediction of N, H and $N_2(A^3\Sigma_u^+,v=0)/N_2(A^3\Sigma_u^+,v=1)$ in a 0.01 H$_2$/0.99 N$_2$ mixture. The discharge parameter is the same as the N$_2$ mixture. The good agreement validates the numerical methods and kinetic model used in this work. With 1% H$_2$ addition, Figure S7(a) shows that the N number density accounts for one fourth of that in the pure N$_2$ plasma shown in Figure S5. This is because N radicals are primarily consumed by H via reaction $N + H + M = NH + M$. H is primarily produced via quenching of electronically excited...
$N_2(A_3^{\Sigma_u^+}, v=0-7)$, $N_2(a^\prime)$, $N_2(C)$ and $N(2D)$ via $N_2(A_3^{\Sigma_u^+}, v=0-7)/N_2(a^\prime)/N_2(C) + H_2 \rightarrow N_2 + H + H$ and $N(2D) + H_2 \rightarrow NH + H$. Similar to the results in $N_2$ plasma shown in Figure S6, at the beginning of the 150-pulse discharge burst, $N_2(A_3^{\Sigma_u^+}, v=0)$ and $N_2(A_3^{\Sigma_u^+}, v=1)$ are produced by the quenching of electronically excited $N_2(B)$ and the higher vibrational levels of $N_2(A_3^{\Sigma_u^+}, v)$ via $N_2(A_3^{\Sigma_u^+}, v=3) + N_2 \rightarrow N_2(A_3^{\Sigma_u^+}, v=1) + N_2(v=1)$, $N_2(B) + N_2 \rightarrow N_2(A_3^{\Sigma_u^+}, v=1) + N_2$ and $N_2(A_3^{\Sigma_u^+}, v=2) + N_2 \rightarrow N_2(A_3^{\Sigma_u^+}, v=0) + N_2(v=1)$. They give rise to $N$ production via $N_2(A_3^{\Sigma_u^+}, v) + N_2(A_3^{\Sigma_u^+}, v) \rightarrow N_2 + N + N$. Different of the quenching pathways in $N_2$ plasma by $N$ atoms, the $N_2(A_3^{\Sigma_u^+}, v)$ concentration declines via $N_2(A_3^{\Sigma_u^+}, v) + H \rightarrow N_2 + H$ due to the efficient $H$ production with $H_2$ addition.

**Figure S7.** TALIF measurement from Yang et al.\textsuperscript{13} and prediction in the present model of (a) $N$ number density as a function of pulse number and (b) $H$ number density as a function of time during a 150-pulse burst with a pulse repetition rate of 100 kHz in a 0.01 H$_2$/0.99 N$_2$ plasma discharge at 150 Torr.
Figure S8. Time evolutions of (a) $N_2(A^3Σ^+_{u, v=0})$ and (b) $N_2(A^3Σ^+_{u, v=1})$ number densities of the TDLAS measurement from Yang et al.\textsuperscript{13} and the model prediction in the present work during a 150-pulse burst with a pulse repetition rate of 100 kHz in a 0.01 H\textsubscript{2}/0.99 N\textsubscript{2} plasma discharge at 150 Torr.

Including the above validations, the other validations about the H\textsubscript{2} plasma sub-mechanism, N\textsubscript{2} plasma sub-mechanism, and H\textsubscript{2}/N\textsubscript{2}/NH\textsubscript{3} gas phase sub-mechanism in the full N\textsubscript{2}/H\textsubscript{2} plasma chemistry are summarized in Table S2. Note that these sub-mechanisms are applicable to H\textsubscript{2}- and N\textsubscript{2}-containing mixtures and are able to provide good predictions for species in plasmas, though their validation reaction systems are different.
Table S2. Summary of model validation in different systems.

<table>
<thead>
<tr>
<th>Model</th>
<th>Validation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full N₂/H₂ plasma chemistry</td>
<td>N, H, NH₃</td>
<td>13, this work</td>
</tr>
<tr>
<td></td>
<td>N₂(A³Σ⁺,v=0), N₂(A³Σ⁺,v=1),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>H₂ plasma sub-mechanism</td>
<td>H₂/O₂/He plasma for H₂ and temperature</td>
<td>8</td>
</tr>
<tr>
<td>N₂ plasma sub-mechanism</td>
<td>N₂ plasma for N, N₂(A³Σ⁺,v=0-2), and</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>N₂(A³Σ⁺,v=4,5);</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄/N₂ plasma;</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>NH₃/O₂/N₂ plasma</td>
<td>15</td>
</tr>
<tr>
<td>H₂/N₂/NH₃ gas phase sub-</td>
<td>Widely validated in H₂/NH₃/N₂⁻ containing</td>
<td>22, 26</td>
</tr>
<tr>
<td>mechanism</td>
<td>mixtures</td>
<td></td>
</tr>
</tbody>
</table>

Before leaving this section, it is noteworthy that, although the model involves 50 species over 494 reactions, not all reactions are important or sensitive to the validation data. Moreover, many reactions/species are correlated and not independent, which allows us to significantly simplify the validation. In other words, if we can validate key reactions/species, then the other reactions/species depending on these key reaction/species will be appropriately validated. For example, N and H are key species, and many other reactions are directly correlated to N and H production, e.g., e + N₂ → e + N + N(²D) and N + H₂(v=2) → NH + H.

6. Numerical modeling of micro-discharges

To simulate the AC DBD plasma, the method developed by van ‘t Veer et al.²⁷,²⁸ is incorporated in our hybrid ZDPlasKin-CHEMKIN model. As the plasma generated by AC DBD is filamentary, the model simulates the filaments or micro-discharges by applying periodic triangular pulses in power density. The experimentally measured plasma power is divided over the different pulses. In this work, the micro-discharges were mimicked by applying the discharge power density over 200/250 triangular pulses with a pulse duration of 400 ns at 20/25 kHz discharge frequency over the total residence time. Here the pulse duration of 400 ns was chosen based on the electric measurements of the pulse duration of peak discharge power. These measurements were performed using a voltage probe (Tektronix, P6015A), a current monitor (Pearson 6585) and an oscilloscope (Tektronix TDS 2012B), similar to Section 1 in this Supporting Information. The reduced electric field is calculated by the following equations.

The discharge power density $P$ deposited into plasma is calculated by
\[ P = jE = eN_e \nu_d E = eN_eN_e^2 \mu_e (E/N)^2 \quad (S11) \]

where \( E \) is the electric field, \( e \) the electron charge, \( N_e \) the electron number density, \( \nu_d \) is the electron drift velocity, and \( \mu_e \) the electron mobility at a given reduced electric field.

Then the reduced electric field \( E/N \) is obtained by

\[ \frac{E}{N} = \frac{1}{N} \sqrt{\frac{P}{eN_0 \mu_e}} \quad (S12) \]

The electron impact rate constant is the function of \( E/N \) which is calculated by the BOLSIG+\(^1\)\(^\text{12}\). Therefore, the electron density calculated from the electron impact ionization, recombination, and attachment rates is a function of \( E/N \), i.e., \( N_e = f(E/N) \). From the equations (S11) - (S12), it can be derived that the discharge power is the function of \( E/N \). At the beginning of the calculation, an initial electron density of \( 10^{10} \text{ cm}^{-3} \)\(^\text{29}\) is used. The initial corresponding \( E/N \) is calculated by equation (S12). Then, the corrected \( E/N \) and electron density will be adapted from the input power density after a few timesteps.

Figure S9 shows the applied discharge power density and the corresponding reduced electric field \( E/N \) of each micro-discharge in a 0.9 \( \text{N}_2/0.1\text{H}_2 \) AC plasma discharge at 20 kHz and 18 kV.

\[ \text{Figure S9. Applied discharge power density and calculated reduced electric field } E/N \text{ in a micro-discharge in a } 0.9 \text{N}_2/0.1\text{H}_2 \text{ AC plasma discharge at } 20 \text{ kHz and } 18 \text{ kV. The pressure is } 100 \text{ Torr.} \]

7. Sensitivity analysis

Sensitivity analysis is a useful and systematic method to quantitatively determine the relationship between the solution to a model and the various parameters that appear in the model’s definition\(^3\)\(^\text{10}\). To
understand the plasma kinetics on the N, H and NH₃ production, the sensitivity coefficient $S_{i,j}$ is solver by (S13),

$$S_{i,j} = \frac{\partial \ln X_i}{\partial \ln k_j}$$

(S13)

The coefficient represents the flux (N and H) or mole fraction change (NH₃) in $X_i$, which is caused by the rate constant $k$ change of reaction $j$. In this work, the reaction rate constant is increased by a factor of 2. The positive sensitivity coefficients indicate the promotive effects on species production, and vice versa.

Figure S10 presents sensitivity coefficients of the elementary reactions involving electrons and excited species for NH₃ production in a 0.9 N₂/0.1H₂ AC plasma discharge at 20 kHz and 18 kV.

8. Vibrational energy transfer validation

To validate the role of vibrational energy transfer on species production, different models with various pathways are conducted. Five additional models with different vibrational energy transfer processes are compared including the full model (model 1) developed in this work, i.e. (2) without V-V' exchange; (3) without V-T relaxation, (4) without chemical abstraction reactions, and (6)
without both V-V' and V-V exchanges. The V-T relaxation, V-V/V-V' exchanges and chemical abstraction processes consist of the reactions involving both H_2(v) and N_2(v). Figure S11 shows the N and H number densities as well as NH_3 mole fraction at varying voltages and frequencies by using different models. The results show that without V-V' energy transfer (model (2)) the model has the similar prediction ability as the full model (model 1) when the voltage is below 14 kV. This is because most of H_2(v) produced by V-V' exchange with N_2(v=2-8) (such as H_2 + N_2(v=2-8) → H_2(v=1) + N_2(v=0-6)) converts back to the lower vibrational level via V-V' exchange with N_2(v=0-7) via H_2(v=1) + N_2(v=0-7) → H_2 + N_2(v=1-8). However, with higher voltage/discharge power (above 14 kV), the discrepancy becomes significant due to more vibrationally excited species production. A considerable number of H_2(v) are still produced via V-V' exchange. Excluding V-V' exchange underpredicts the NH_3 formation. Without V-V exchange (model 3) or V-T relaxation (model 4), the NH_3 concentration is over-predicted while the N number density is under-predicted as shown in Figure S11. This is caused by the over prediction of H_2(v=2, 3) concentration when some quenching pathways of N_2(v) and H_2(v) to the lower vibrational level and ground states are missing, such as V-V exchange N_2(v=2) + N_2 → N_2(v=1) + N_2(v=1) and V-T relaxation N_2(v=2) + H_2 → N_2(v=1) + H_2. Without chemical abstraction reaction of vibrationally excited species (model 5), the NH_3 concentration is under-predicted due to the lack of N + H_2(v=2)/H_2(v=3) → NH + H. Figure S11 also clearly shows that without V-V/V-V' (model 6) the model fails to predict the N number density and NH_3 concentration. This is because the concentrations of the vibrationally excited species are not accurately predicted without correctly considering the vibrational energy transfer process.

The above comparison results show that the N and H number densities and NH_3 concentration can only be well-predicted by including vibrational energy transfer, i.e., the V-V/V-V' exchange, V-T relaxation, and chemical abstraction reactions of vibrationally excited species.
Figure S11. Experimental results and model predictions with different vibrational energy transfer processes for N and H number densities as well as NH₃ mole fraction at varying voltages and frequencies in a 0.9 N₂/0.1 H₂ AC plasma discharge.
9. Electron energy transfer

Figure S12 shows the fractions of electron energy deposition into different excitation modes as a function of $E/N$ in N$_2$ (dashed line) and 0.9 N$_2$/0.1H$_2$ (solid line) mixtures. It can be seen from Fig. S12 that most discharge energy is deposited to the excitation of N$_2$(v) and H$_2$(v) under $E/N = 200$ Td (the $E/N$ range of micro-discharges in this study). Especially, when the $E/N$ is below 30 Td, the energy that H$_2$(v) gains ranges from ~5% to ~20%. The above energy deposition leads to the energy exchanges of V-V (i.e., H$_2$(v)-H$_2$(v)) and V-V’ (N$_2$(v)-H$_2$(v)), which eventually enhance the coupling between N and NH for the final ammonia synthesis.

![Figure S12](image)

Figure S12. Fractions of electron energy deposition into different excitation modes as a function of $E/N$ in N$_2$ (dashed line) and 0.9 N$_2$/0.1 H$_2$ (solid line) mixtures. (Tr+rot: translational and rotational excitation; v: vibrational excitation; el: electronic excitation; dis: dissociation; ion: ionization). The energy loss fractions are calculated by BOLSIG$^{+12}$.

References


