Plasma assisted reforming for enhanced ammonia ignition and reduced NOx emissions

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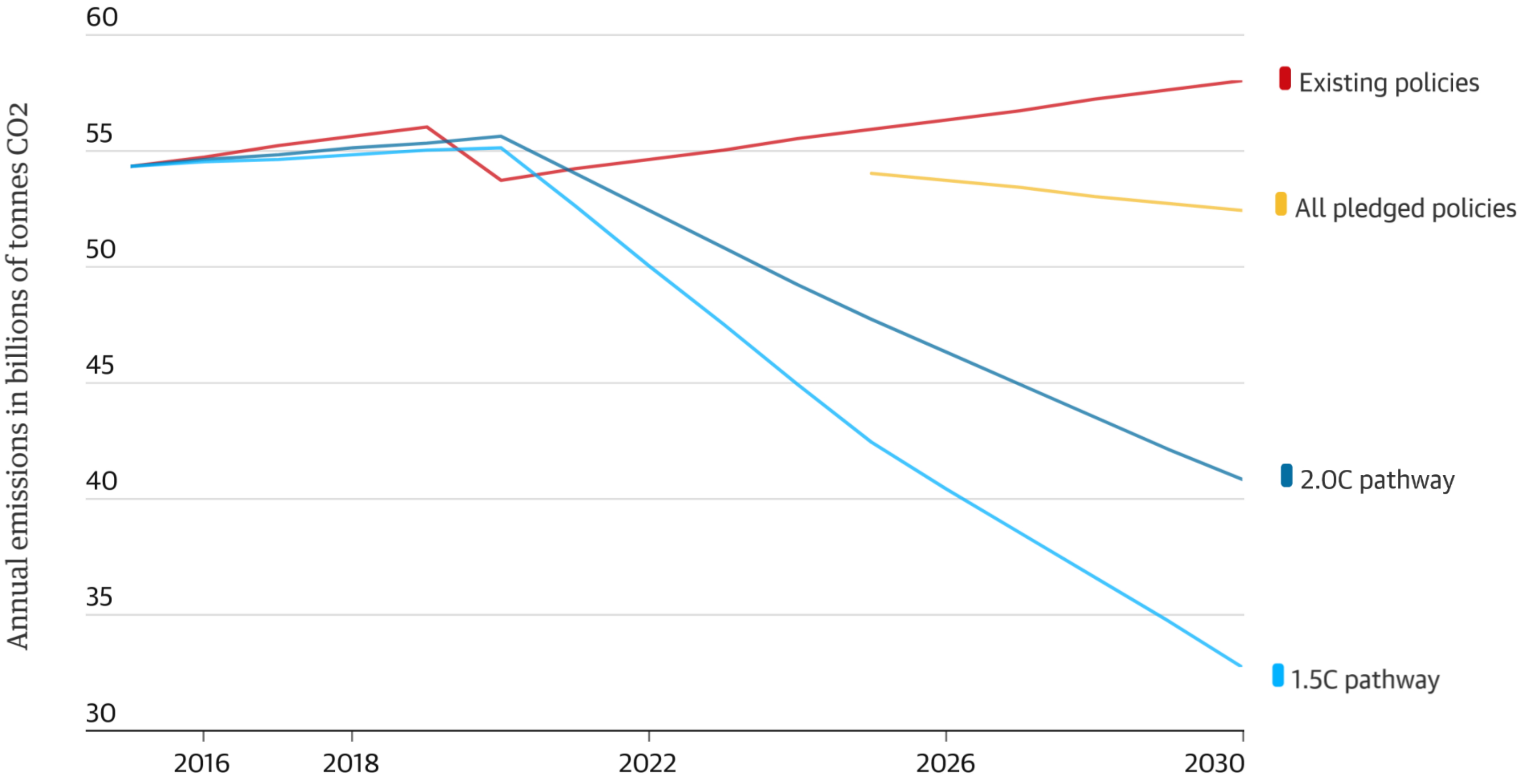
No credible pathway to 1.5°C in place

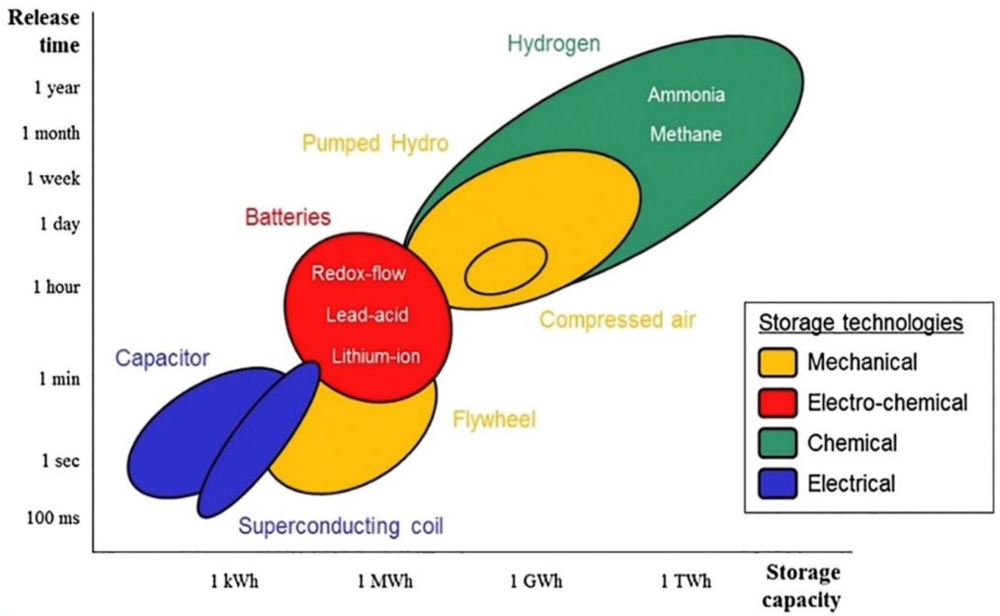


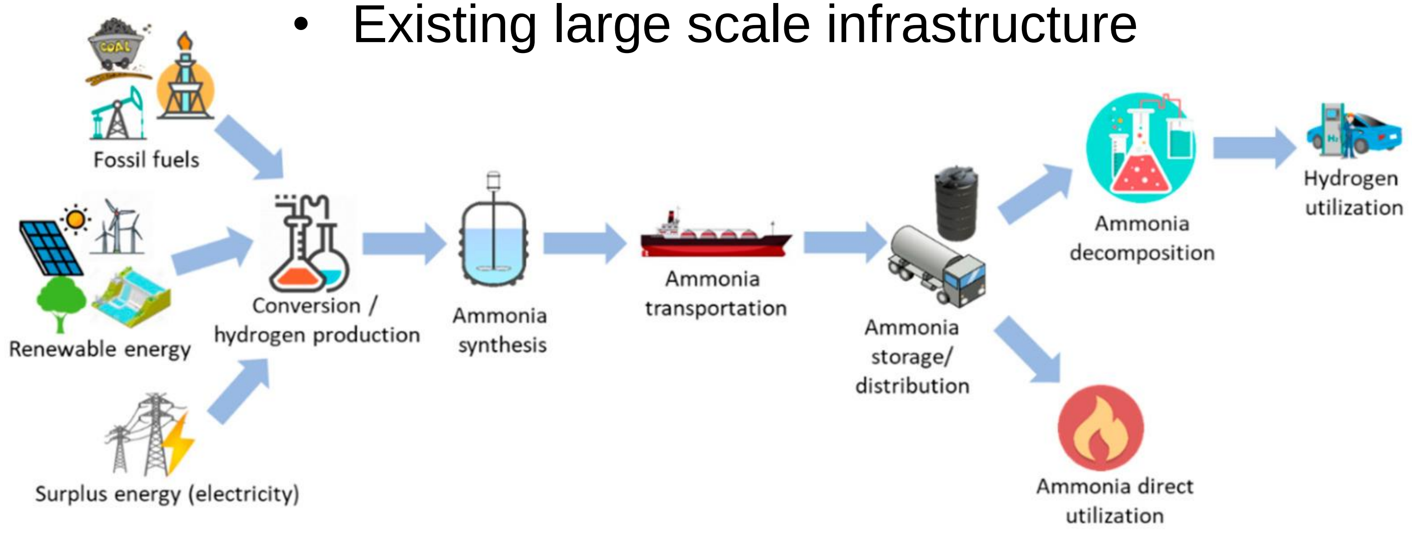
Guardian graphic | Source: UNEP

Ammonia for Energy Storage

- Renewable energy: solar and wind are cheap but intermittent
- Storage is key in the transition
- Chemical storage of H_2 in NH_3:
  - Carbon free
  - High energy density
  - Easily stored, stable
  - Relatively safe
  - Existing large scale infrastructure

Ye et al. 2017

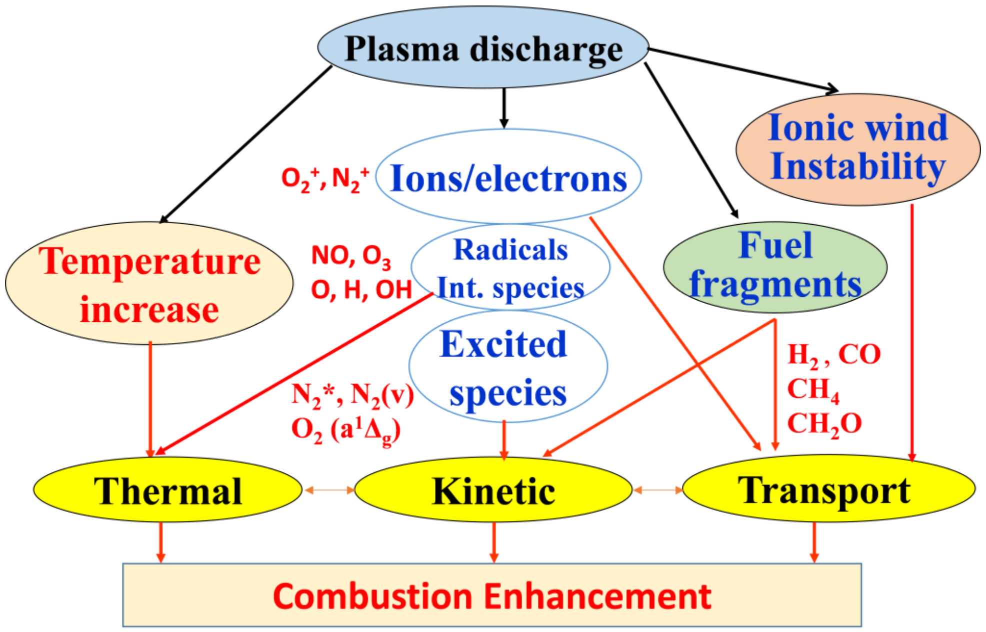




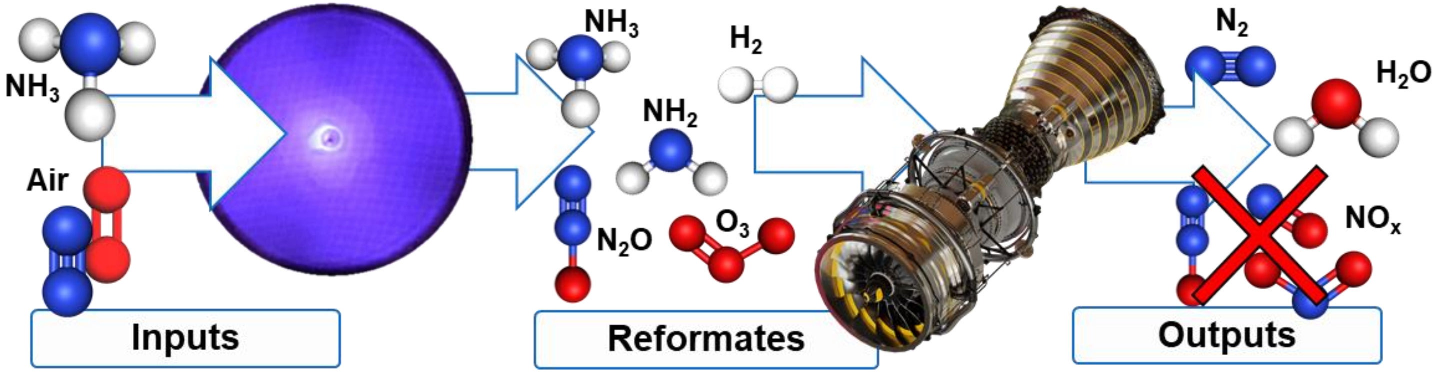
Plasma Chemistry and Ammonia

Problems with burning ammonia:
- Resistant to ignition
- Low flame speed (≈7 cm/s)
- High NOx emissions
- Narrow flammability limits

Plasma capabilities:
- Enhance ignition
- Stabilize combustion - wider flammability limits
- Reduce NOx emissions
- On-demand and flexible
- Small % of combustion energy



Ju and Sun, *PECS* 48 (2015)



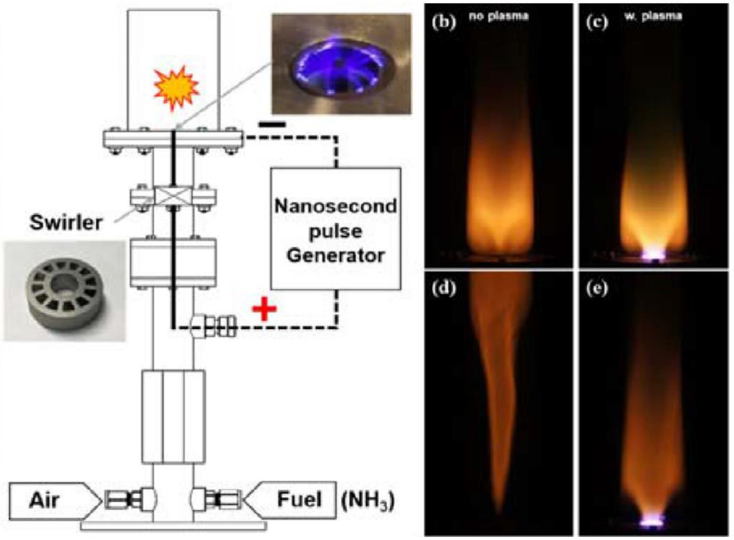
Background: PAC Ammonia

Some experimental studies:

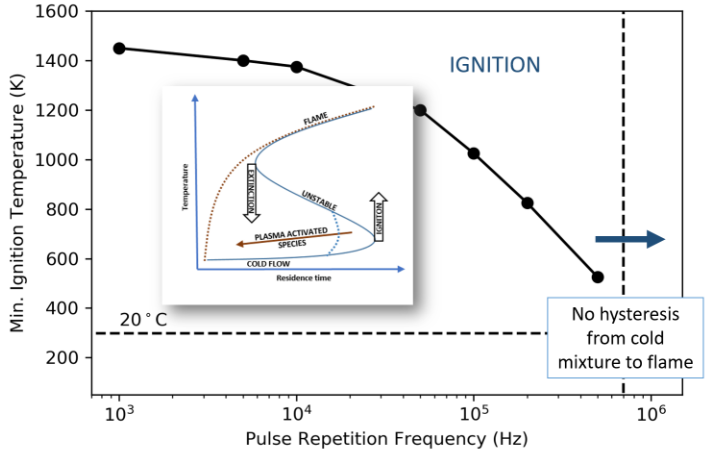
- Choe et al. (2021, 2022): ns pulsed discharge in a swirl combustor using NH_3/air:
  - Lean blow-off extension
  - NOx reduction at lean mixtures
- Lin et al. (2022), Tang et al. (2022): GAP burner with stable flames and low NOx

Some numerical studies:

- Shioyoke et al. (2018): increased laminar flame speed with plasma reforming
- Faingold and Lefkowitz. (2021, 2022): enhanced flammability and shortened ignition delay time, reduced NOx
- Taneja and Yang (2022): shorter ignition delay and reduced NOx



Choe et al., *Combust. Flame* 228 (2021)

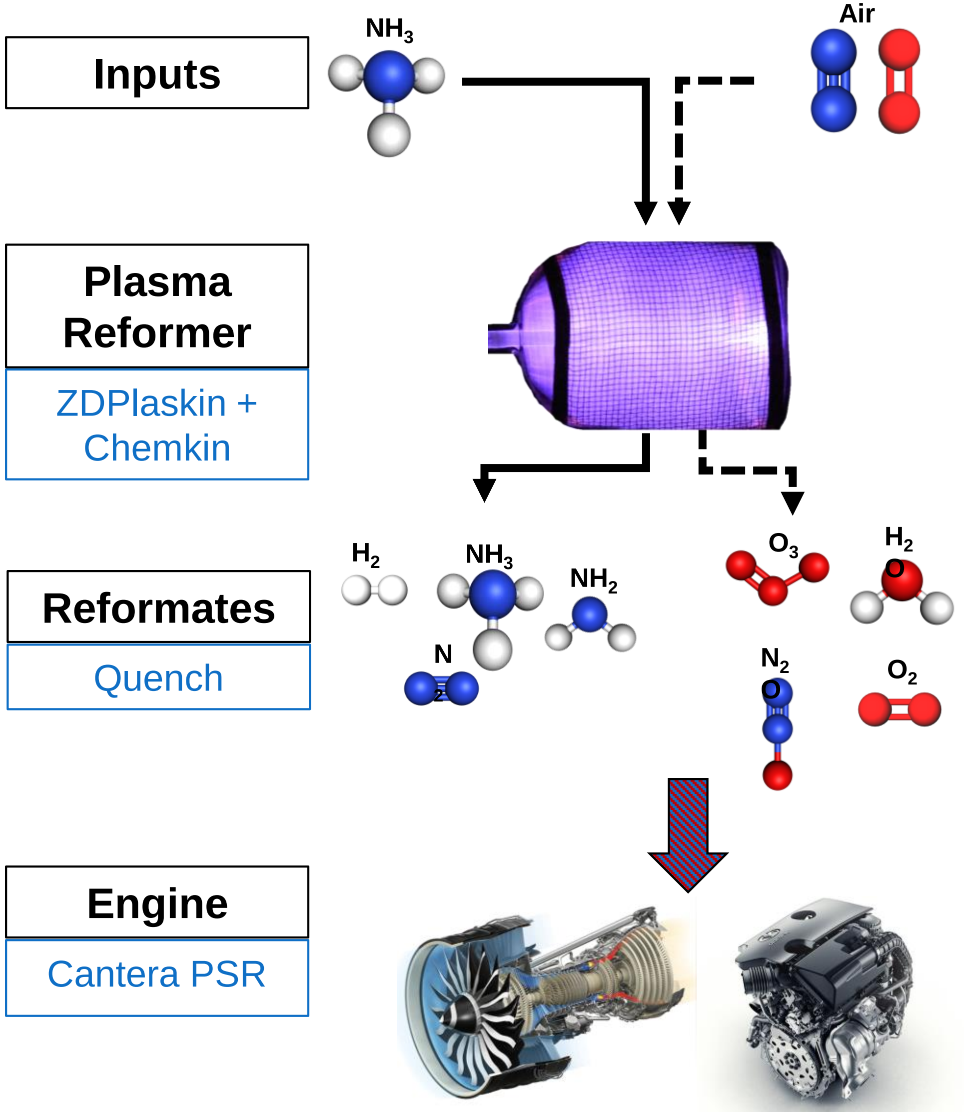


Faingold and Lefkowitz, *PRCI* 38 (2021)

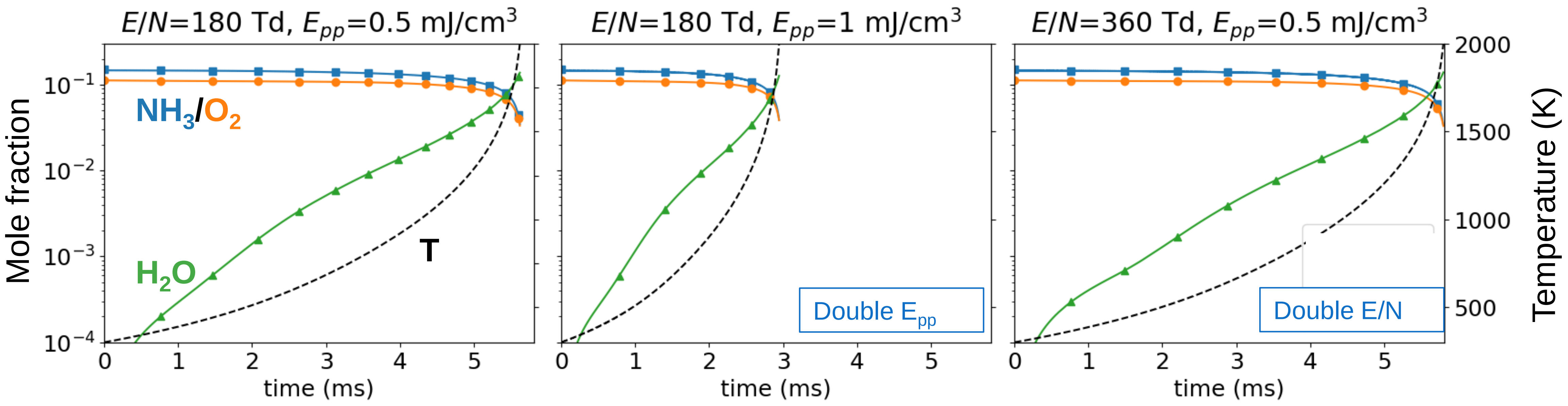
Plasma-reforming of Ammonia and Mixtures

Two-step plasma reforming & ignition simulations

1. Plasma reforming to H_2 and other species (e.g. NH_2)
   - 0D plasma chemistry of $NH_3/O_2/N_2$
   - Combination of ZDPlaskin and Chemkin
   - Extension of Faingold & Lefkowitz, *PROCI* 2021 model to include N_2 dilution
2. All excited species quenched
   - Neutral species maintained, including radicals
3. Reformates injected into "engine"
   - 0D ignition simulations, P = 5 MPa, T_i = 925 K, ϕ = 1
   - Cantera PSR using Xiao, Valera-Medina, and Bowen 2017 model



Plasma Parameters for Reforming

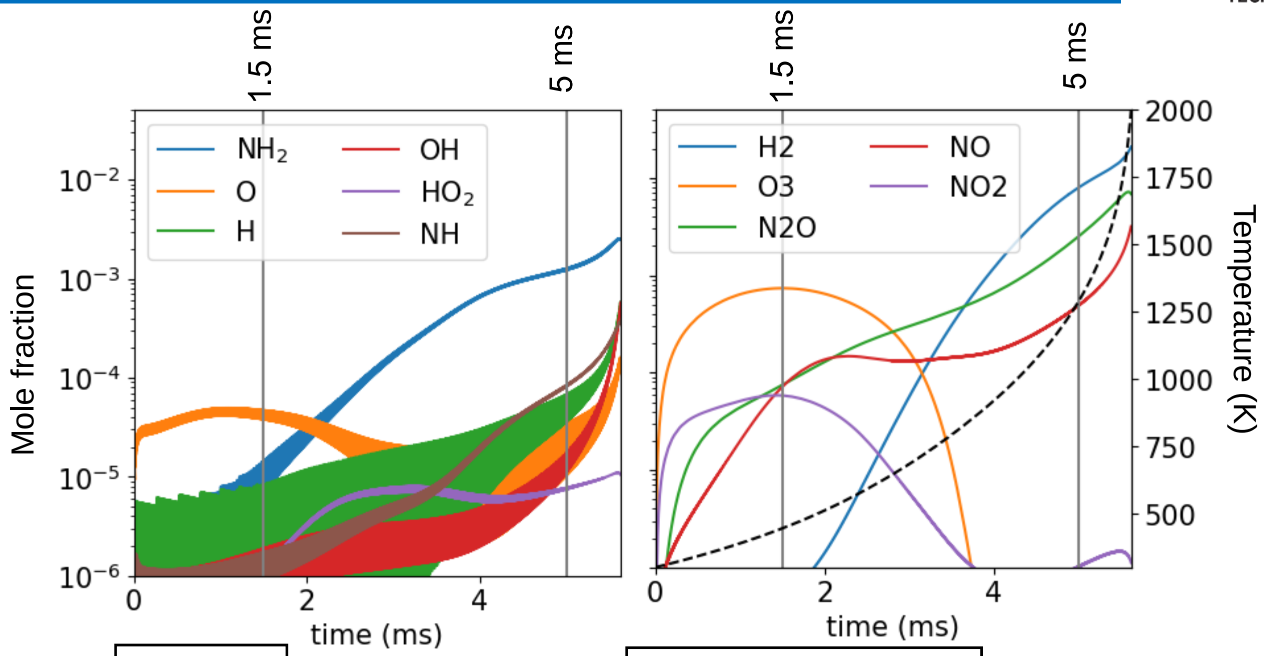


Major species and temperature evolution of stoichiometric $NH_3/O_2/N_2$ reforming

- Pulse repetition frequency, PRF: Determines residence time τ
  - Low PRF = $\tau \uparrow$, minor effect on species distribution
  - High PRF = $\tau \downarrow$, limit at $\tau > \tau_{\text{ignition}}$
  - PRF = 200 kHz is reasonable for 10 ms residence time
- Energy per pulse, E_{pp}: Halves reforming time for e_{pp} = 0.5 → 1 mJ/cm^3
- Reduced electric field, *E/N*: No significant effect on reforming for E/N = 180 → 360 Td

$NH_3/O_2/N_2$ Plasma Reforming

- Minor species and temperature evolution
  - E/N = 180 Td
  - PRF = 200 kHz
  - E_{pp} = 0.5 mJ/cm^3
- Conditions for optimal reforming for up to 10 ms residence time
- Two conditions chosen for ignition delay predictions:
  - 1.5 ms: maximize O_3
  - 5 ms: maximize H_2



Radicals | **Stable Intermediates**

	Unreformed	1.5 ms	5 ms
τ_{ign} (s)	0.58	0.45	0.01
T_{ad} (K)	2860	2438	2233
X_{NO} (ppm)	5000	1400	200

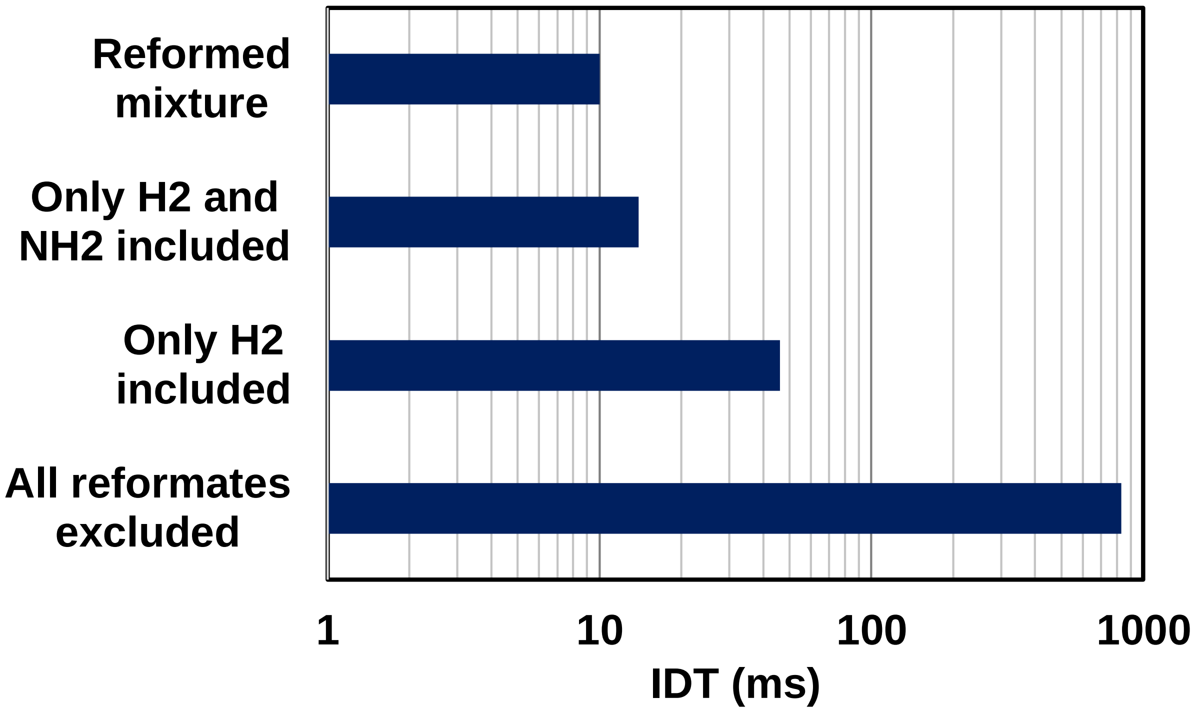
Ignition of a 5 ms reformed mixture:

- 50-fold reduction in ignition delay
- 25-fold reduction in Nox
- Energy input from1000 pulses ≈ 4% of energy from combustion
- Some loss of enthalpy

Reformed Species Sensitivity Analysis

To determine sensitive species, we calculate IDT excluding different reforming products:

- H_2 and NH_2 account for most reduction of ignition delay
  - ≈ 8000 ppm H_2
  - ≈ 1100 ppm NH_2
- All other species from reforming do not have significant impact

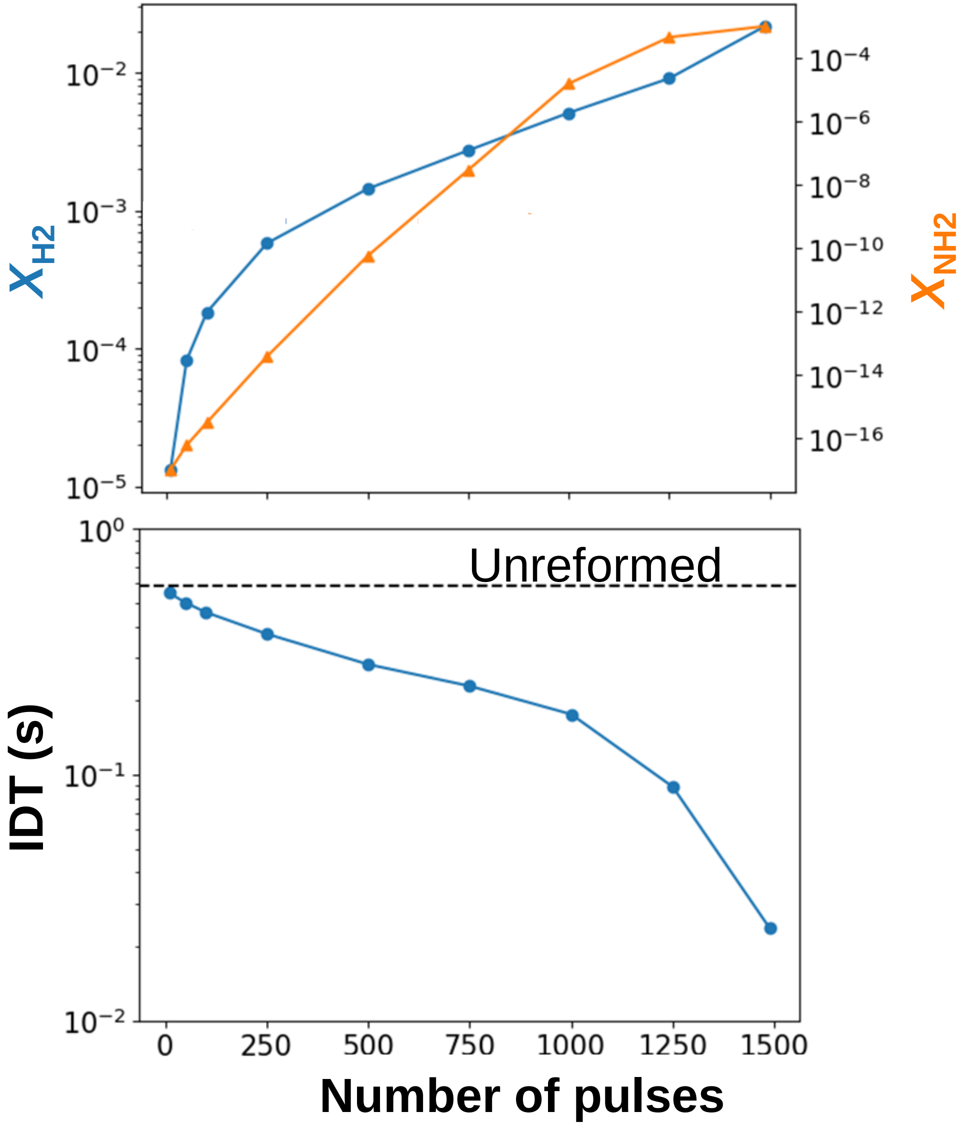


NH_3 Plasma Reforming

Reforming of pure ammonia – main products are H_2 and NH_2:

- E/N = 180 Td
- PRF = 200 kHz
- E_{pp} = 0.5 mJ/cm^3
- N = 1-1500 pulses

- At least 1000 pulses needed to significantly effect ignition delay
- Energy input from 1500 pulses = 750 mJ/cm^3 ≈ 6% of energy from combustion



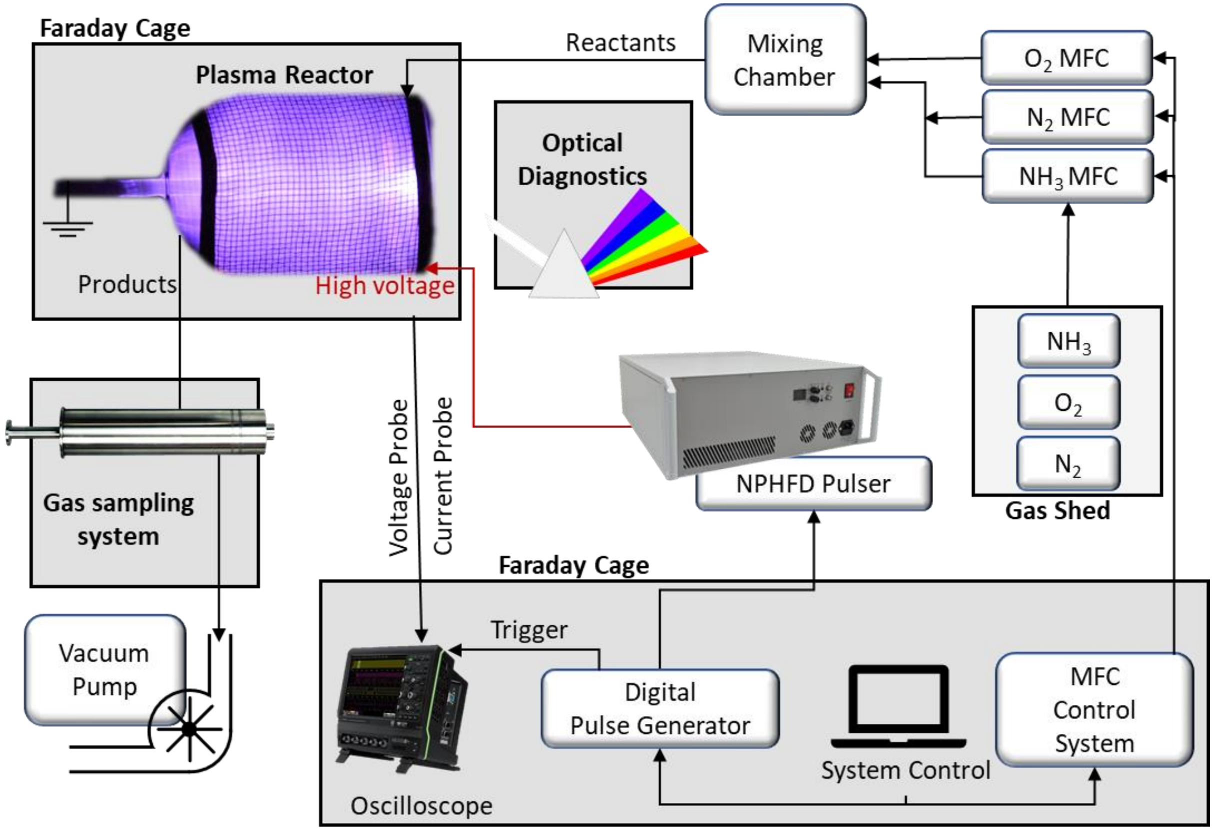
Conclusions, Current & Future Work

Numerical investigation found:

- Ammonia reforming in DBD can reduce ignition delay by x50 at engine-relevant conditions
- The key species affecting ignition delay time are H_2 and NH_2
- NO_x is reduced due to additional NH_2 and HO_2 present after plasma reforming

Next steps:

- Validate model experimentally in a well-stirred, homogenous plasma reactor



Thanks for your Attention!

The Combustion and Diagnostics Lab Group

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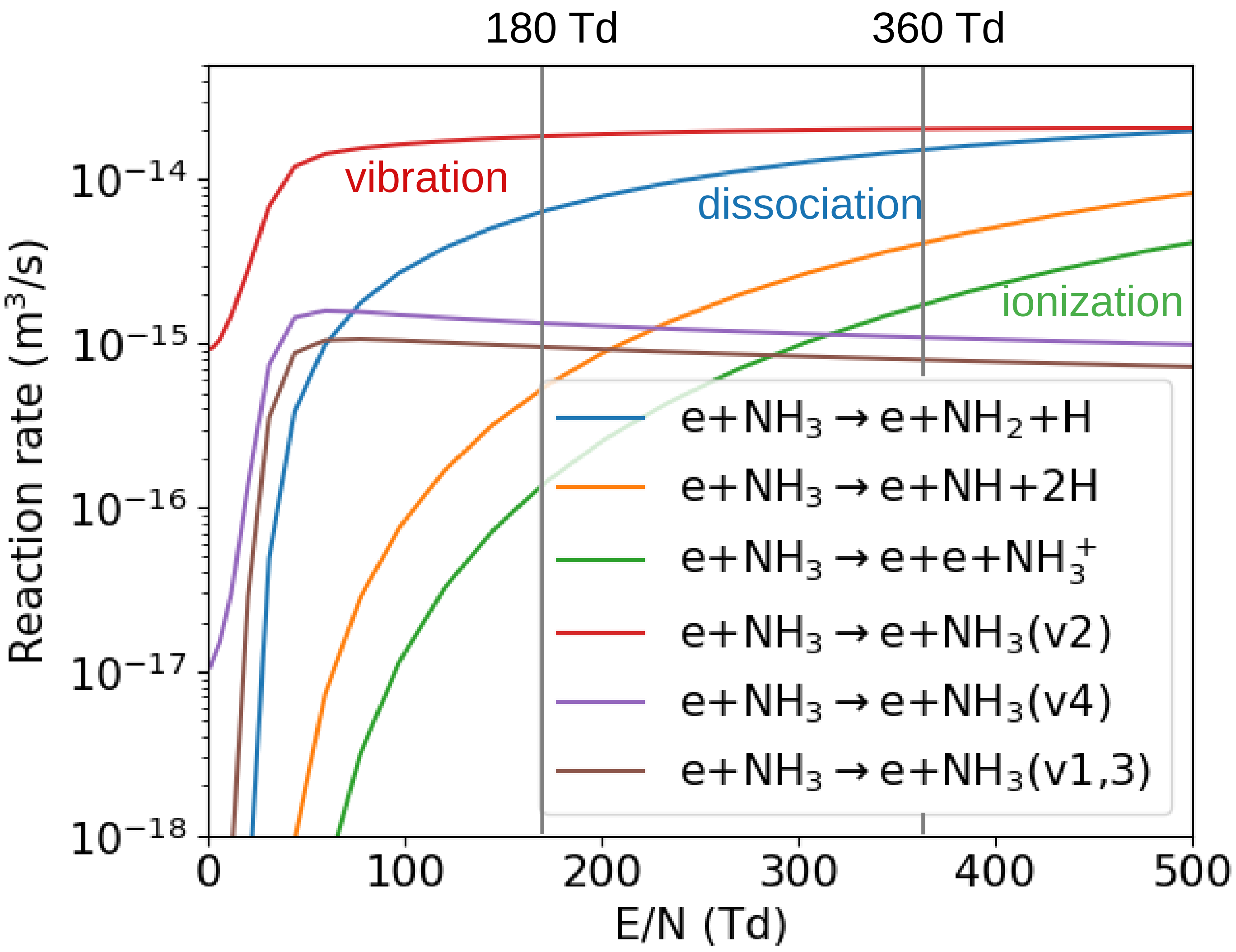
Building a plasma-ammonia combustion kinetic model

Excitation and ionization by electron collision	
O_2	Phelps and Pitchford 1985
N_2	Phelps 1991
NH_3	Hayashi 1987
Excited species reactions	
$H_2/N_2/NH_3$	Carrasco, Herrero, and Tanarro 2012
NH_3/O_2	Ling Wang et al. 2004
$NH_3(v)$ reactions	Calculated by theory from Fridman 2008
Additional $N_2(v)$ reactions	Calculated by theory from Kable and Knight (2003)
Neutral ground state reactions	
$NH_3/O_2/N_2$	Xiao, Valera-Medina, and Bowen 2017

Plasma Reforming Conditions

- E/N = 180 Td or 360 Td
  - Shifts electron collisions to target NH_3 vibrational excitation or dissociation
- PRF = 5 – 500 kHz
  - Range of plasma PRF available for experiments
- E_{pp} = 0.5 – 1 mJ/cm^3
  - Pulse energies realistic for DBD discharges with diffuse plasma



Plasma Chemistry Solver

$$\frac{dN_i}{dt} = \sum_{j=1}^{j_{max}} Q_{ij}(t) \quad (1)$$

$$P_{ext} = P_{elec} + P_{gas} + P_{chem} \quad (2)$$

$$P_{ext} = j' \times E = e \times N_e \times v_{dr} \times E = e \times N_e \times N^2 \times \mu_e \times (E/N)^2 \quad (3)$$

$$P_{elec} = \frac{3}{2}\,kB\,\frac{d(N_e T_e)}{dt} \quad (4)$$

$$P_{gas} = \frac{\gamma}{\gamma - 1}\,kB\,\frac{d(NT)}{dt} \quad (5)$$

$$P_{chem} = \sum_i \varepsilon_i \frac{dN_i}{dt} \quad (6)$$

(7)

$$(\rho_i^{n+1} - \rho_i^n)/\Delta t = \omega_i^{plasma} + \omega_i^{combustion} \quad (8)$$

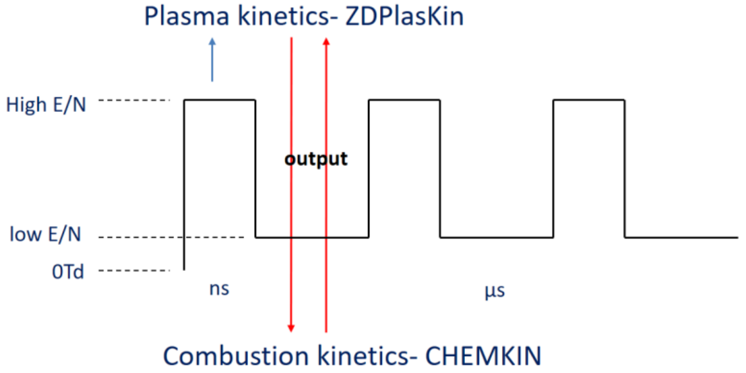
$$(T^{n+1} - T^n)/\Delta t = \Delta T_{plasma} + \Delta T_{combustion} \quad (9)$$

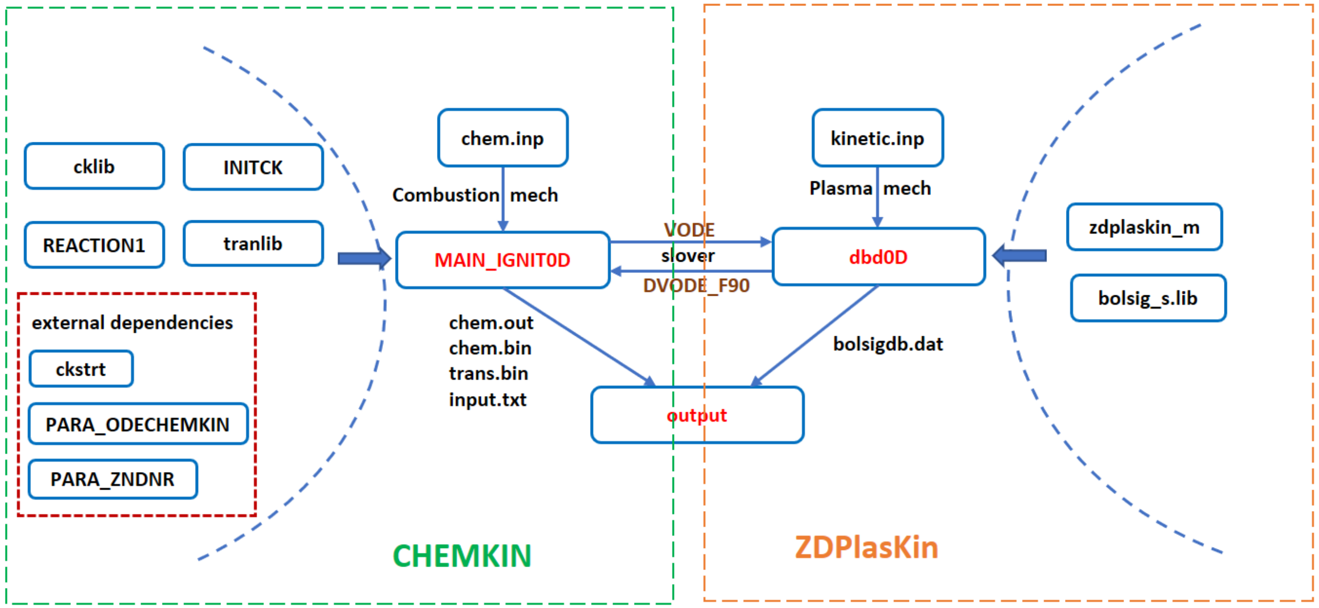
$$(\rho_i^{n+1} - \rho_i^*)/\Delta t = \omega_i^{plasma} \quad (10)$$

$$(\rho_i^* - \rho_i^n)/\Delta t = \omega_i^{combustion} \quad (11)$$

$$(T^{n+1} - T^*)/\Delta t = \Delta T_{plasma} \quad (12)$$

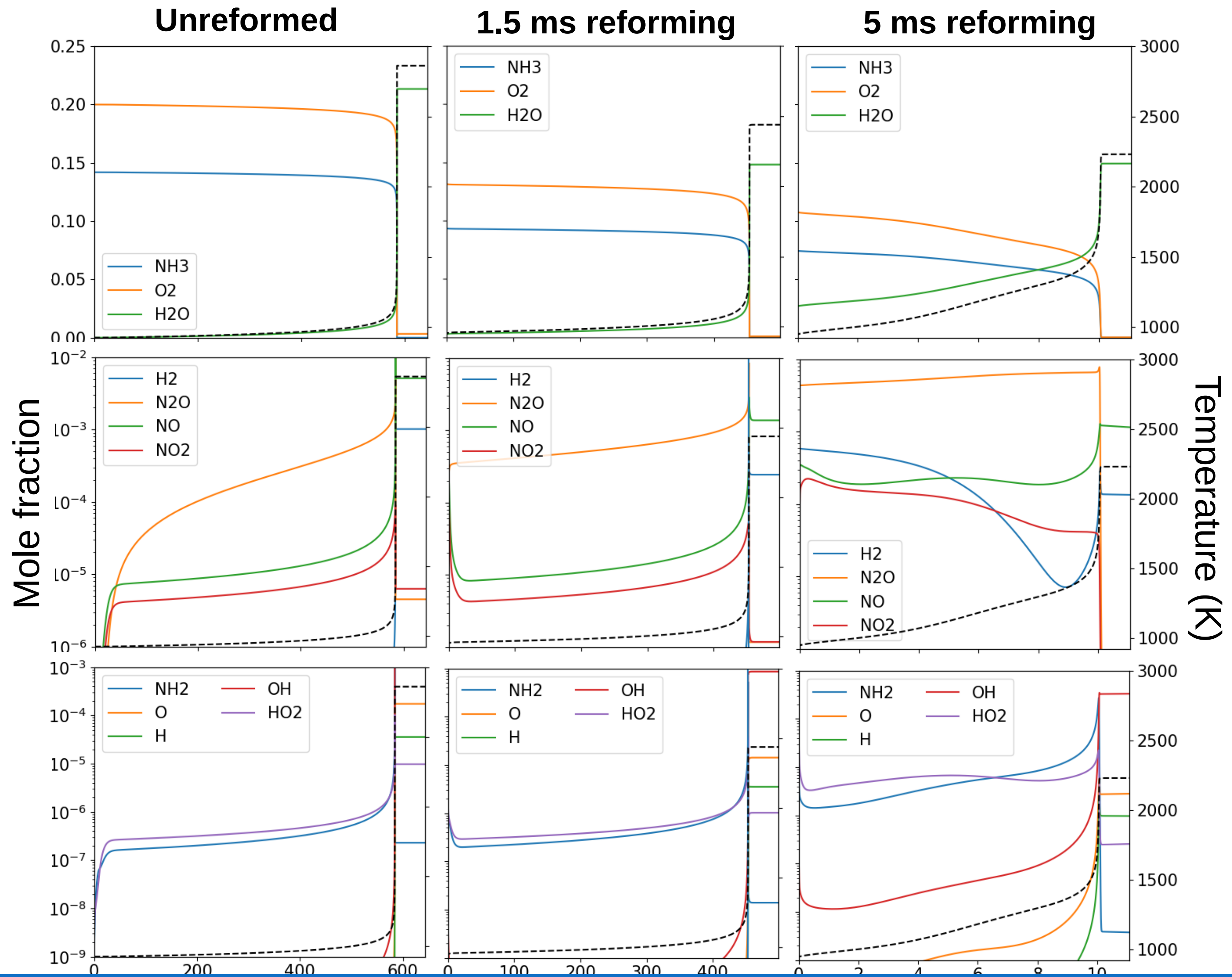
$$(T^* - T^n)/\Delta t = \Delta T_{combustion} \quad (13)$$





Pancheshnyi, et al., *Bulletin of the American Physical Society* 53 (2008)

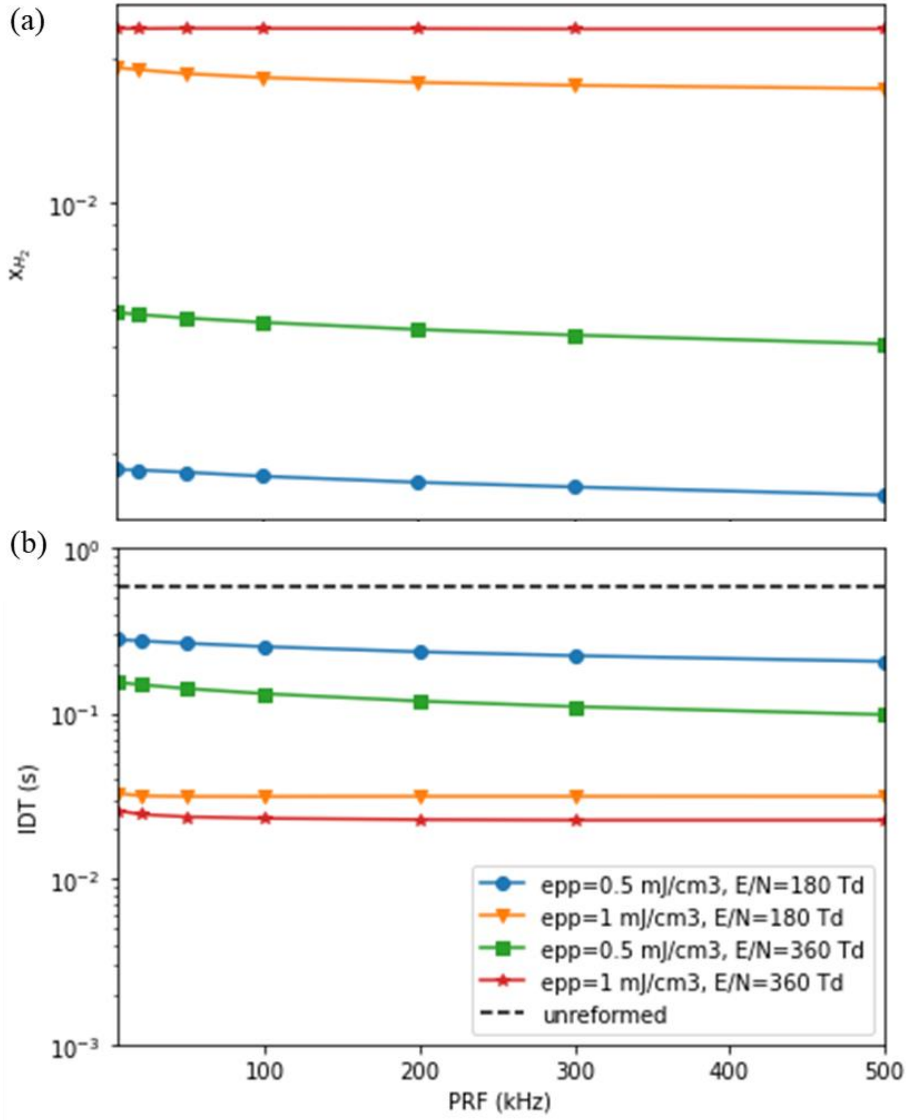
Reformed $NH_3/O_2/N_2$ Ignition



- Unreformed mixture ignition:
  - τ_{ign} = 0.58 s
  - T_{ad} = 2860 K
  - $X_{NO} \approx$ 5000 ppm
  - Impractical ignition delay
- 1.5 ms reforming:
  - τ_{ign} = 0.45 s
  - T_{ad} = 2438 K
  - $X_{NO} \approx$ 1400 ppm
  - Not significantly different from thermal case
- 5 ms reforming:
  - τ_{ign} = 0.01 s
  - T_{ad} = 2233 K
  - $X_{NO} \approx$ 200 ppm
  - 50-fold reduction in ignition delay
  - 25-fold reduction in Nox
  - Energy input from1000 pulses $\approx$ 4% of energy from combustion

NH_3 Plasma Reforming

- E/N = 180 Td or 360 Td
- PRF = 5 – 500 kHz
- e_{pp} = 0.5 and 1 mJ/cm^3
- N=700 pulses.
  - To compare between similar energy inputs, each reforming simulation ran for the same amount of pulses and varying residence times.
- Conversion to H_2 increases with e_{pp} and E/N, but not strong function of PRF (apart from residence time considerations)



Path Flux Analysis (Ignition)

- Path flux analysis at 10% τ_{ign} for thermal and plasma reforming
- Overall rates x200 for plasma case
- Most important reaction:

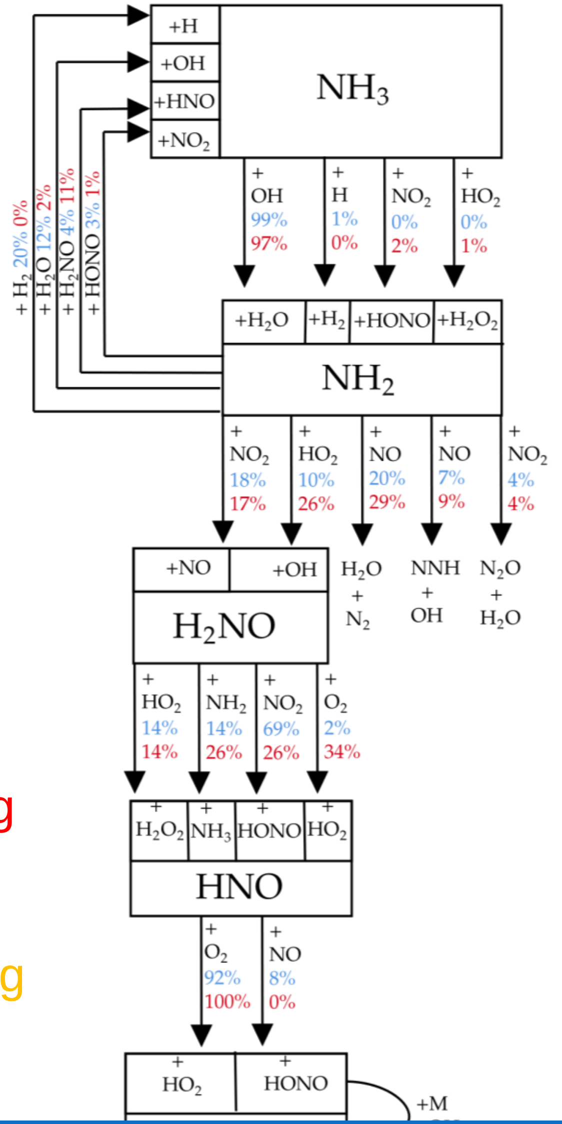
$$\mathbf{NH_3 + OH \rightarrow NH_2 + H_2O}$$

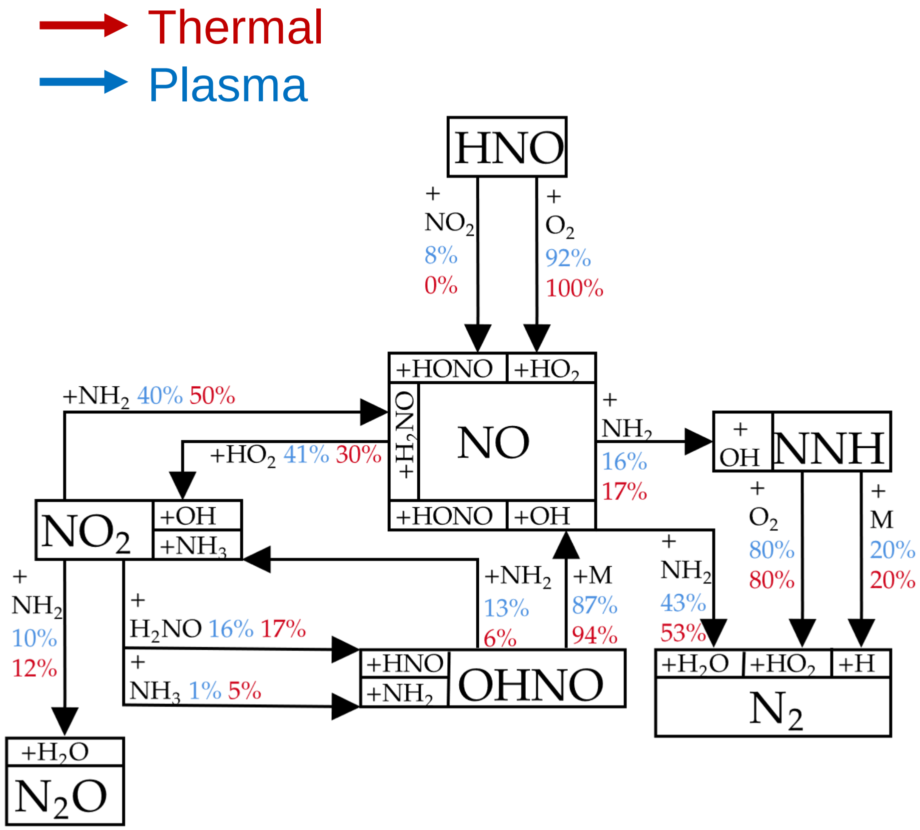
- Pathways of NO consumption are most sensitive in system

$NO + NH_2 \rightarrow N_2 + H_2O$ Terminating

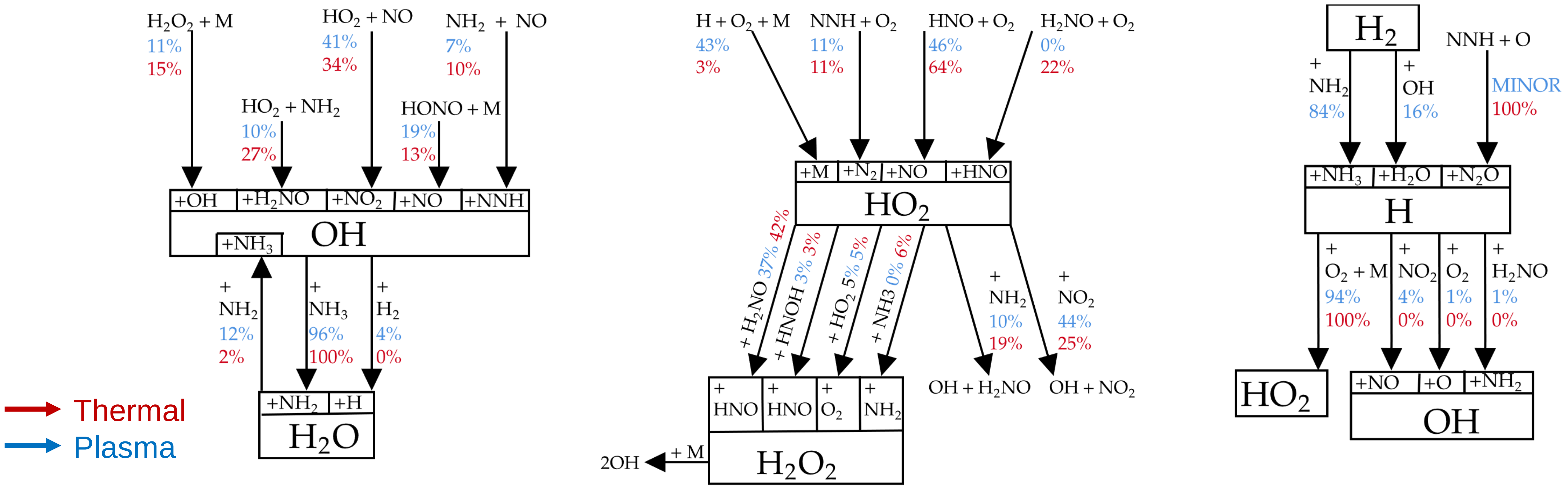
$NO + NH_2 \rightarrow NNH + OH$ Branching

$NO + HO_2 \rightarrow NO_2 + OH$ Propagating





Path Flux and Sensitivity Analysis



- >90% of OH formed from HO_2 (or HO_2 dependent paths: H_2O_2 and HONO)
- Major shift in source of HO_2 from thermal case to plasma case
- Caused by presence of H_2

Reaction Sensitivity Analysis