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Analysis of Methane-Air Edge Flame Structure

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Acknowledgement

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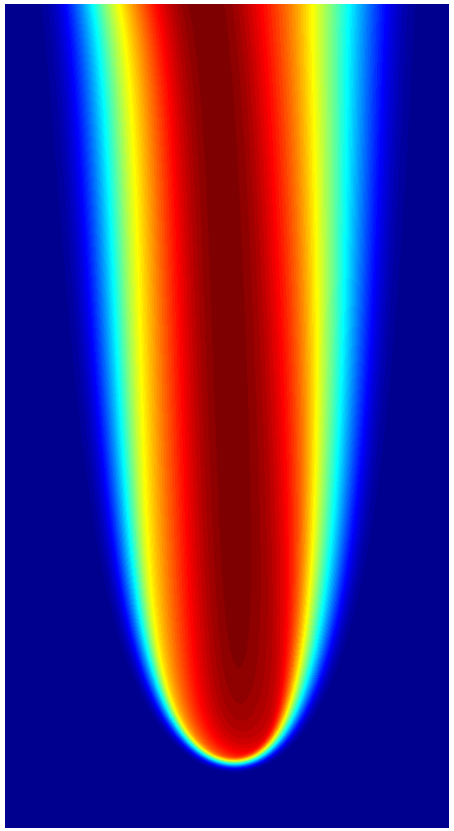
Introduction

- Edge flames are a class of flames that involve both premixed and non-premixed flame physics
- Relevance in microstructure of turbulent combustion
- Edge flame structure
  - Curved premixed flame front; Trailing non-premixed flame
- There have been many studies of edge flames, with a focus on flame stabilization and lift off height characteristics

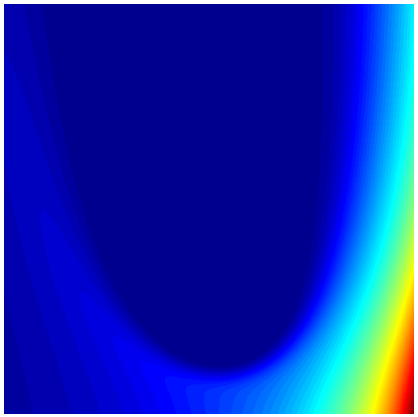
  Takahashi & Katta, 2000; Walsh *et al.*, 2005; Won *et al.*, 2005; Chung, 2007;
- Some studies have probed the chemical structure of Hydrogen and Methane edge flames Takahashi *et al.*, 1998; Im & Chen, 1999;
- We explore the detailed structure of hydrocarbon and nitrogen chemistry in Methane-Air edge flames
  - Identify important processes in different flame regions

Problem Setup

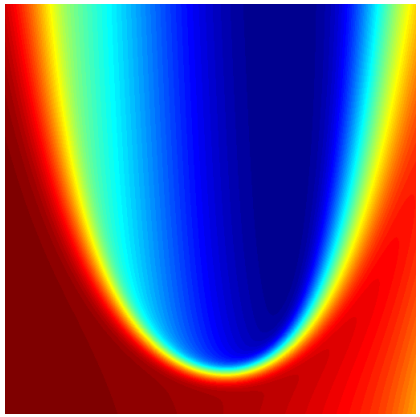
- Low Mach number detailed chemistry reacting flow model
- GRImech3.0 ($N = 53$ species, 325 reactions)
- $\sim 1.5 \times 3.0$ cm domain
- Uniform inflow velocity
- Inflow mixture: mixing layer pure CH4 (right) and Air (left)
  - tanh() mixture fraction profile, $\xi_{st} = 0.055$
  - ξ is the elemental mixture fraction (Bilger)



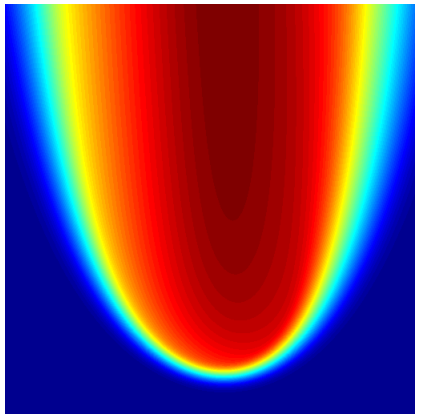
Edge flame detail: Y_i and w_i : CH_4, O_2, T, and NO



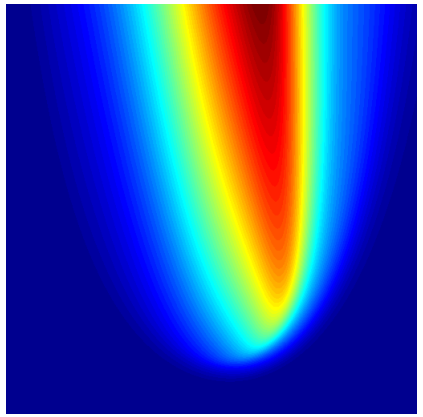
CH_4



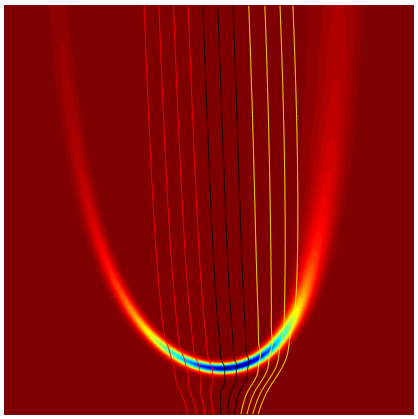
O_2



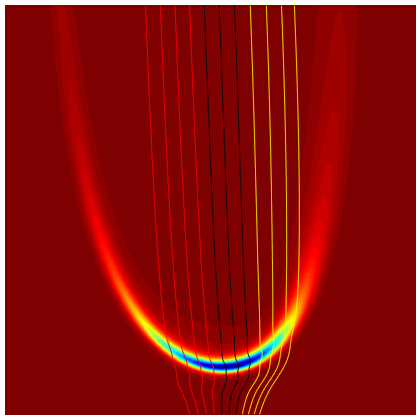
T



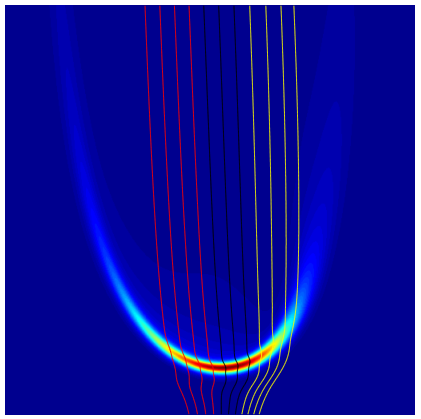
NO



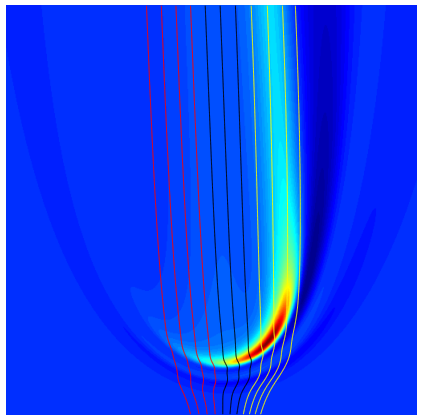
w_{CH_4}



w_{O_2}

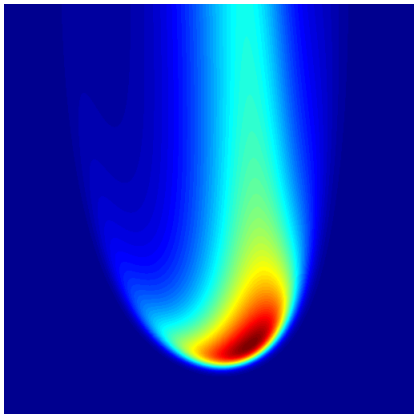


w_T

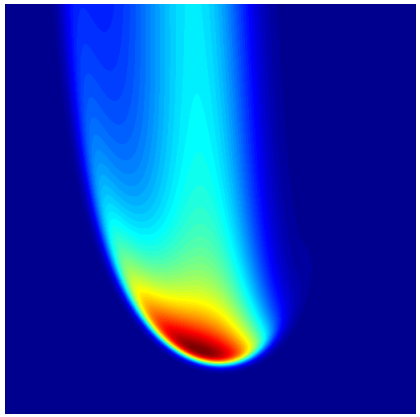


w_{NO}

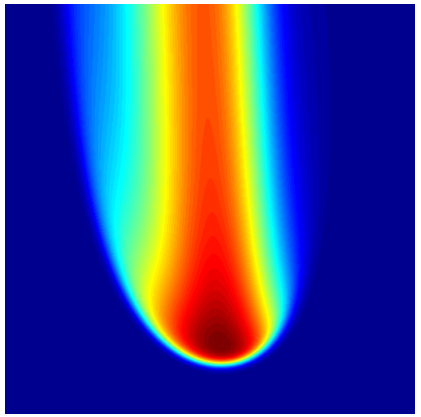
Edge flame detail: Y_i and w_i : H, O, OH, and N



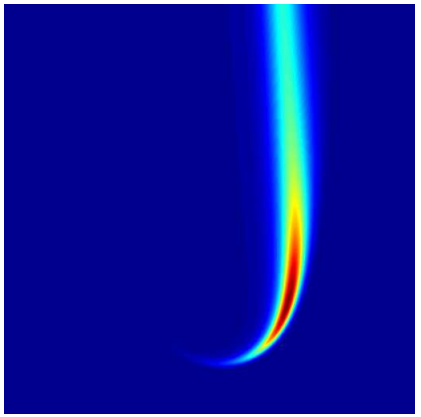
H



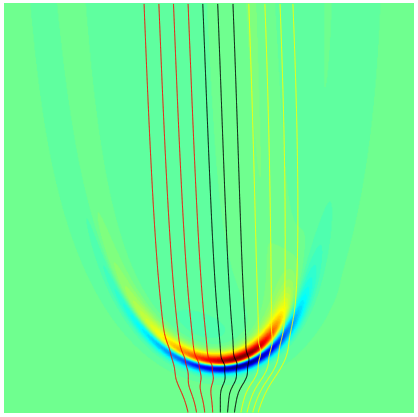
O



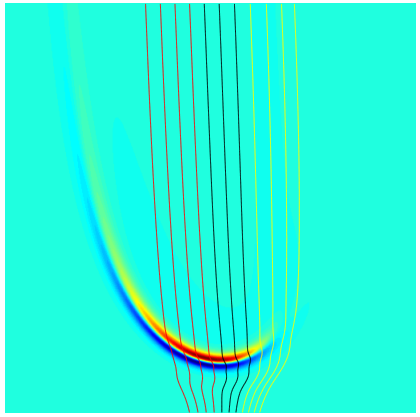
OH



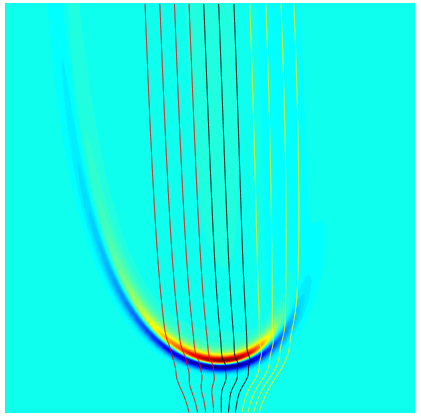
N



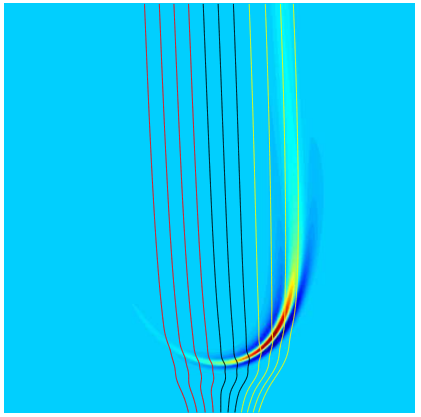
w_{H}



w_{O}



w_{OH}



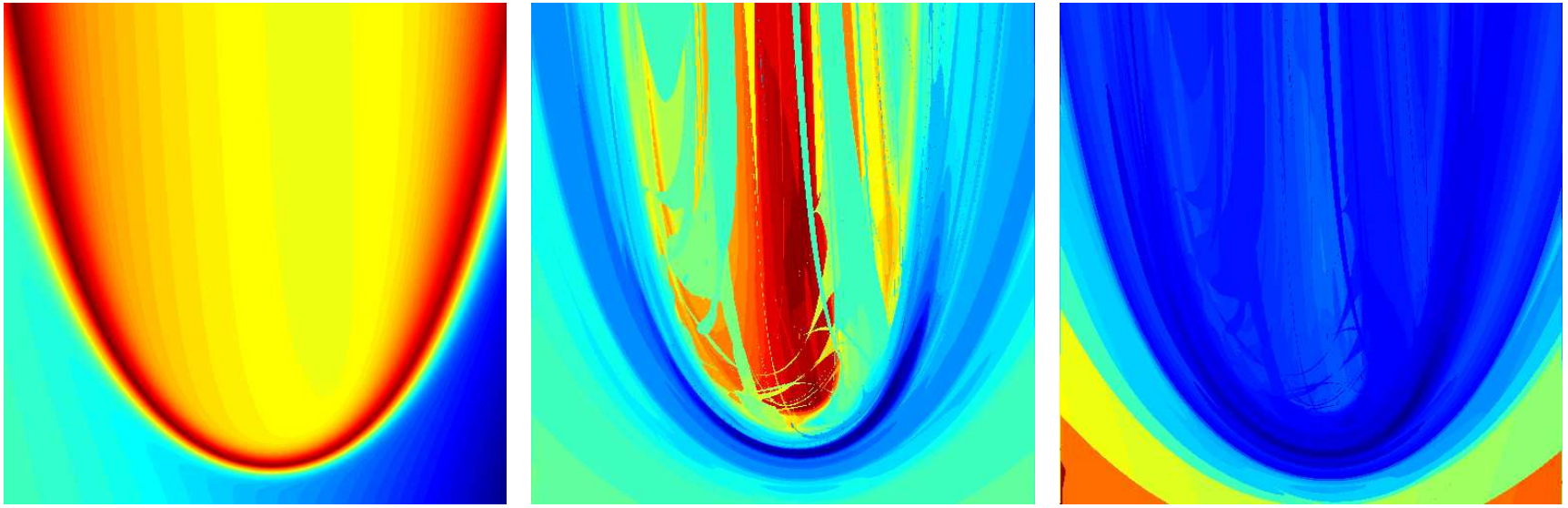
w_{N}

Fast-Slow Structure of Chemical Systems

- Chemical systems are characterized by exterme stiffness
  - Typical range of time scales 1 ms — 1 ns
- Stiff/fast-slow ODE systems exhibit low order behavior
  - Fast processes are "slaved" to the slow processes
  - Slow processes govern evolution of the system along a low dimensional Slow Invariant Manifold (SIM)
- Computational Singular Perturbation (CSP) provides :
  - analysis of the dynamics of a chemical system
  - decoupling of fast and slow processes
  - cause-and-effect relationships
  - means for automated chemical model simplification strategies

Lam and Goussis, 22^{nd} Comb. Symp., 1988.

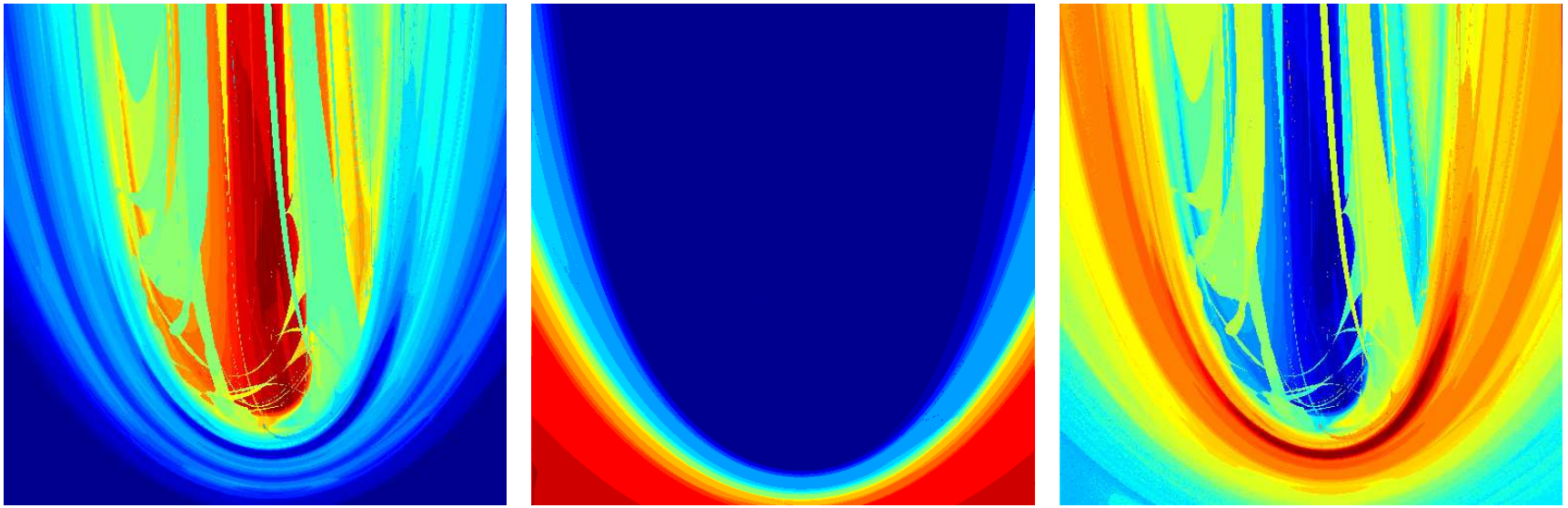
Time Scales and the Fast Subspace Dimension M



τ_1 M τ_{M+1}

- Fastest time scale $\tau_1 \sim \mathcal{O}(1\ \mathrm{ns})$
- Fast subspace dimension M:
  ~ 4 in the premixed reaction zone
  ~ 40 in the diffusion flame behind the edge flame
- Driving time scale (fastest of the slow) τ_{M+1}
  $\sim \mathcal{O}(10\ \mathrm{ns})$ in the premixed reaction zone

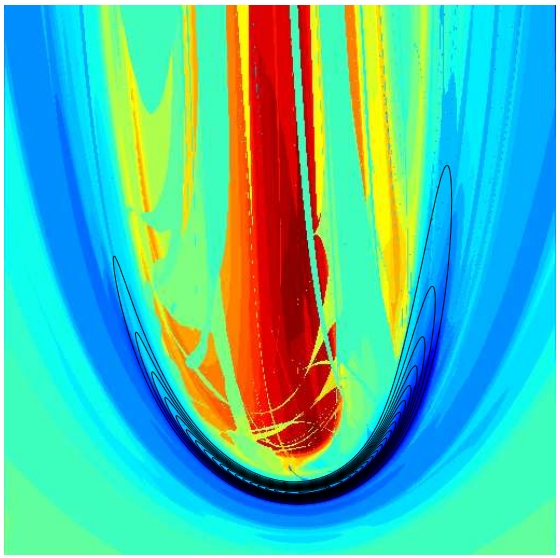
Composition of M — the Fast Subspace Dimension



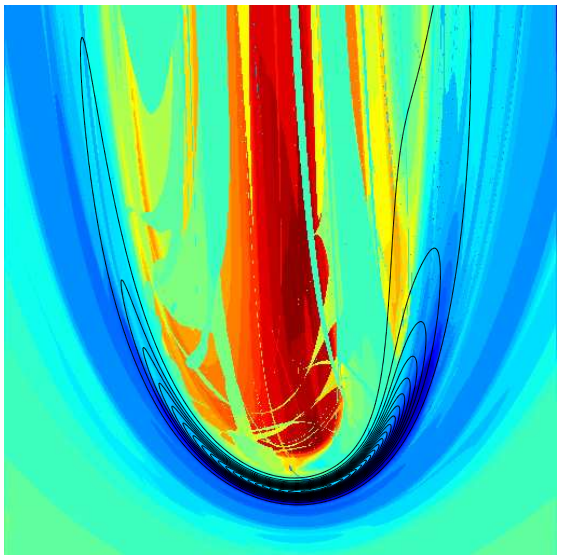
Exhausted Modes # Frozen Modes # Active Modes

- $M =$ (# Exhausted Modes) + (# Frozen Modes)
- # Conservation modes : $N_C = 5$
- # Active Modes $= N - M - N_C$
  - Highest activity in premixed reaction zone

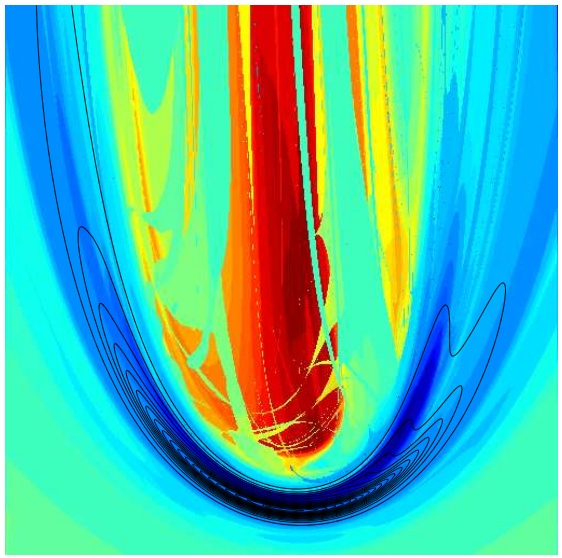
Internal Structure within the Premixed Front



$w_{\mathrm{CH_4}}$



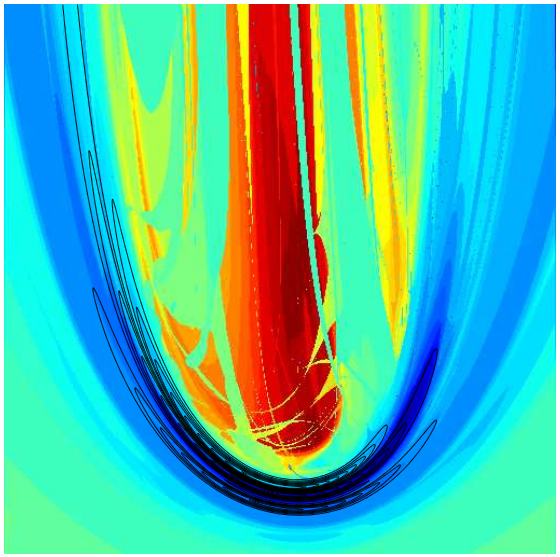
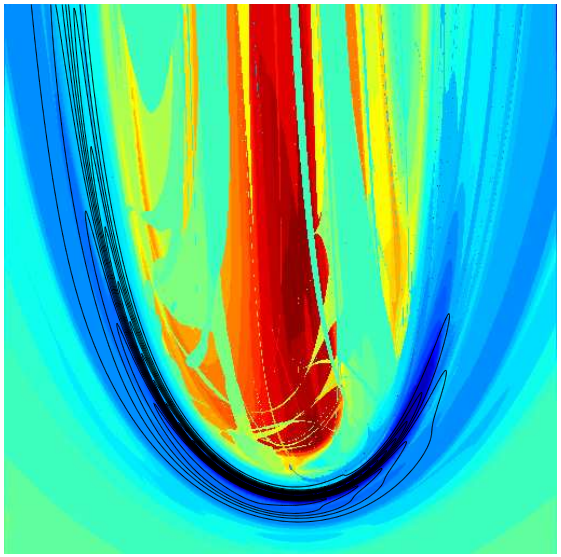
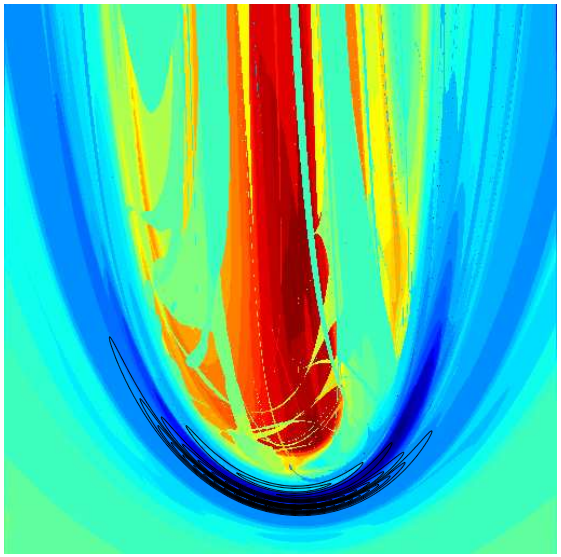
Y_{HCO}



$Y_{\mathrm{CH_3O}}$

- M field indicates a two-layer structure in the premixed front
- The two layers are separated significantly on the rich side
- Internal layer coincides with the main hydrocarbon fuel consumption zone
- High mass fraction of CH_3O in the outer layer

Internal Structure within the Premixed Front

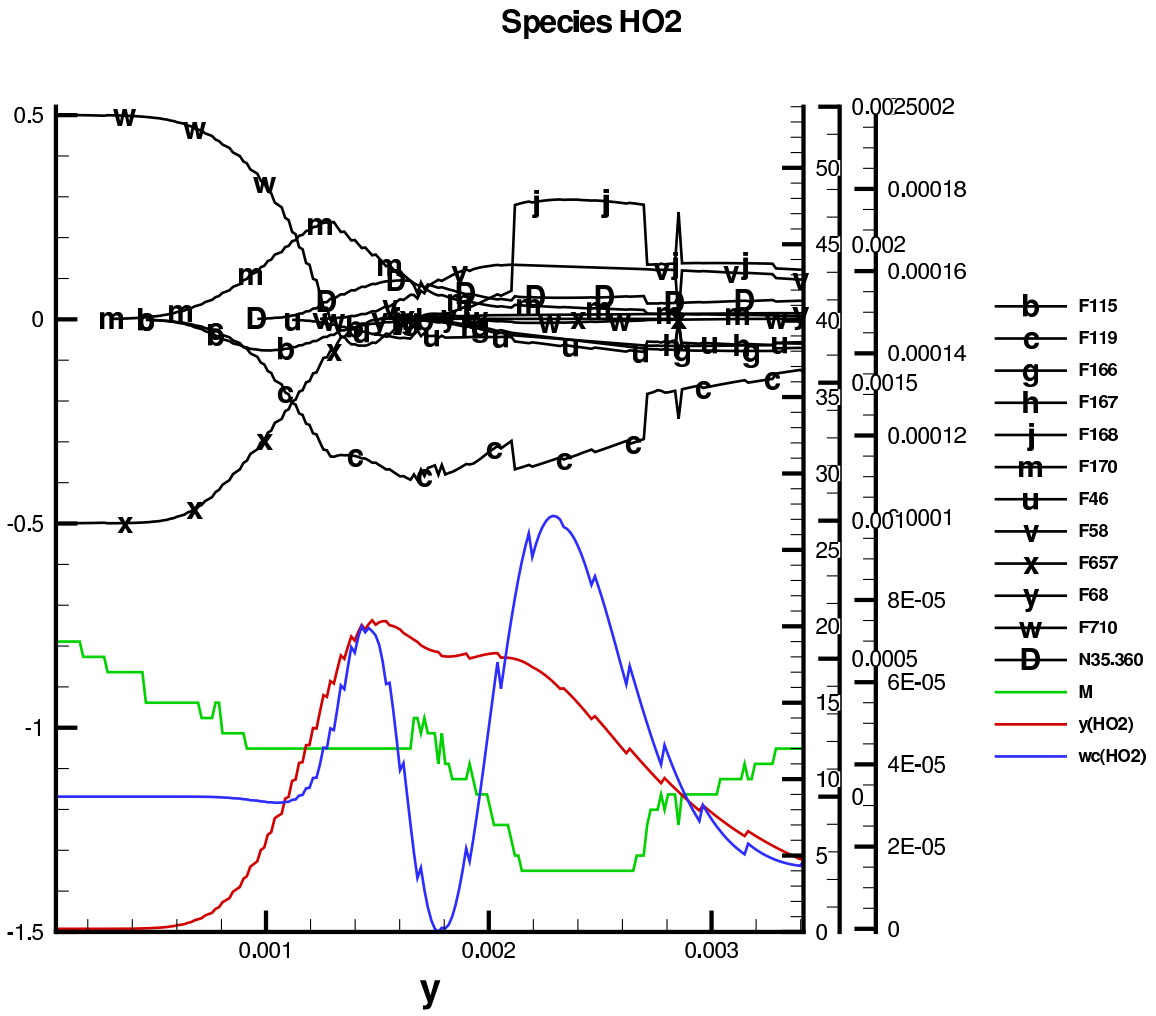




$w_{\mathrm{HO_2}}$ $w_{\mathrm{H_2O_2}}$ $w_{\mathrm{CH_3O}}$

- Outer layer associated with low temperature chemistry
- Participation by HO_2, H_2O_2, and CH_3O reactions
- Why the larger separation on the rich side?
  - Examine flow structure along a $\xi = 0.075$ line in the rich region

HO2 Importance Indices along $\xi = 0.075$

- Two minimum plateaus of M coincide with maxima in $w_{\mathrm{HO_2}}$
- Cold inflow:
  Convection < 0; Diffusion > 0
- Preheat region/First layer:
  Convection $\lesssim 0$; Diffusion $\gtrsim 0$
  R170: $CH_3O+O_2 \rightarrow HO_2+CH_2O$ > 0
  R119: $HO_2+CH_3 \rightarrow OH+CH_3O$ < 0
- Main Premixed front/Second layer:
  R168: $HCO+O_2 \rightarrow HO_2+CO$ > 0
  R119: $HO_2+CH_3 \rightarrow OH+CH_3O$ < 0



Active Timescale and Driving Process Analysis

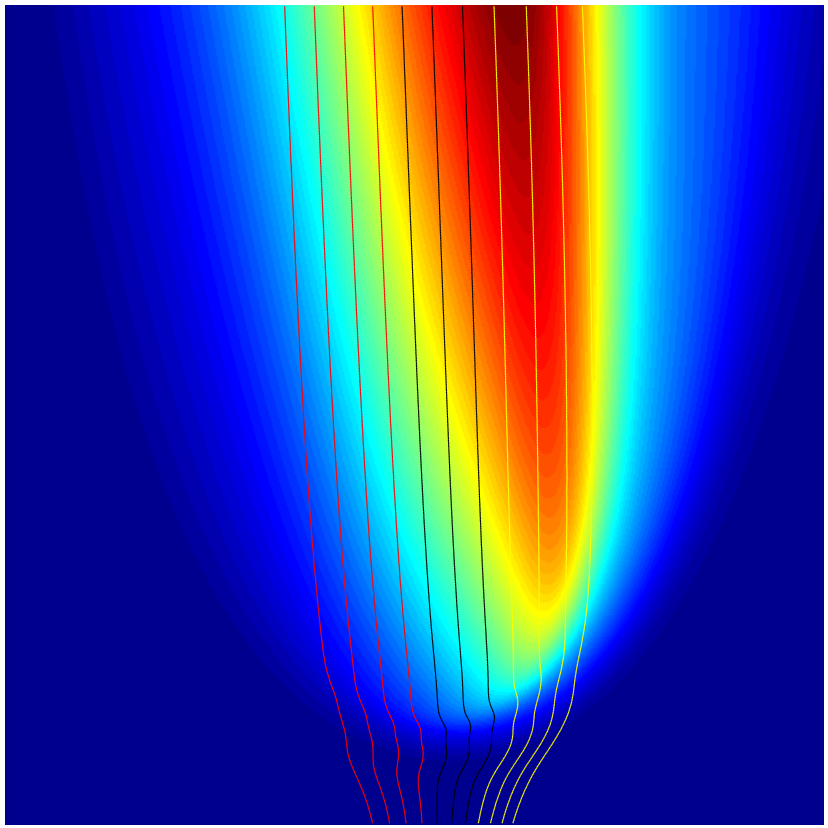
- $\xi = 0.035$: peak $w_{\mathrm{CH_3O}}$: $M = 11$; $T = 749$ K;
  $\tau_{M+1} = 0.2\,\mu\mathrm{sec}$: Rxns w/ highest Part. Indices in P_{M+1}:
  - R176: $\mathrm{HCCO+O_2 \rightarrow OH + 2CO}$ > 0
  - R119: $\mathrm{HO_2 + CH_3 \rightarrow OH + CH_3O}$ > 0
  - R114: $\mathrm{OH + CH_2CO \rightarrow HCCO + H_2O}$ < 0
  - R80: $\mathrm{H + CH_2CO \rightarrow HCCO + H2}$ < 0
- $\xi = 0.075$: Low-T peak $w_{\mathrm{CH_3O}}$; $M = 12$; $T = 692$ K;
  $\tau_{M+1} = 1\,\mu\mathrm{sec}$: Rxns w/ highest Part. Indices in P_{M+1}:
  - R119: $\mathrm{HO_2 + CH_3 \rightarrow OH + CH_3O}$ > 0
  - R46: $\mathrm{H + HO2 \rightarrow 2OH}$ > 0
  - R98: $\mathrm{OH + CH_4 \rightarrow CH_3 + H_2O}$ < 0
  - R84: $\mathrm{OH + H_2 \rightarrow H + H_2O}$ < 0
- On the rich side, low T chemistry is slower than on the lean side, such that a longer residence time is needed for activation of the fast fuel breakdown reactions
  — hence the larger separation between the two M-layers

- Thermal (Zeldovich) mechanism
  - $N + NO = O + N_2$ R178
  - $N + O_2 = NO + O$ R179
  - $N + OH = NO + H$ R180
- Prompt pathway initiated by Rxns of Hydrocarbon radicals with N_2 to produce HCN and N, which are converted to NO:

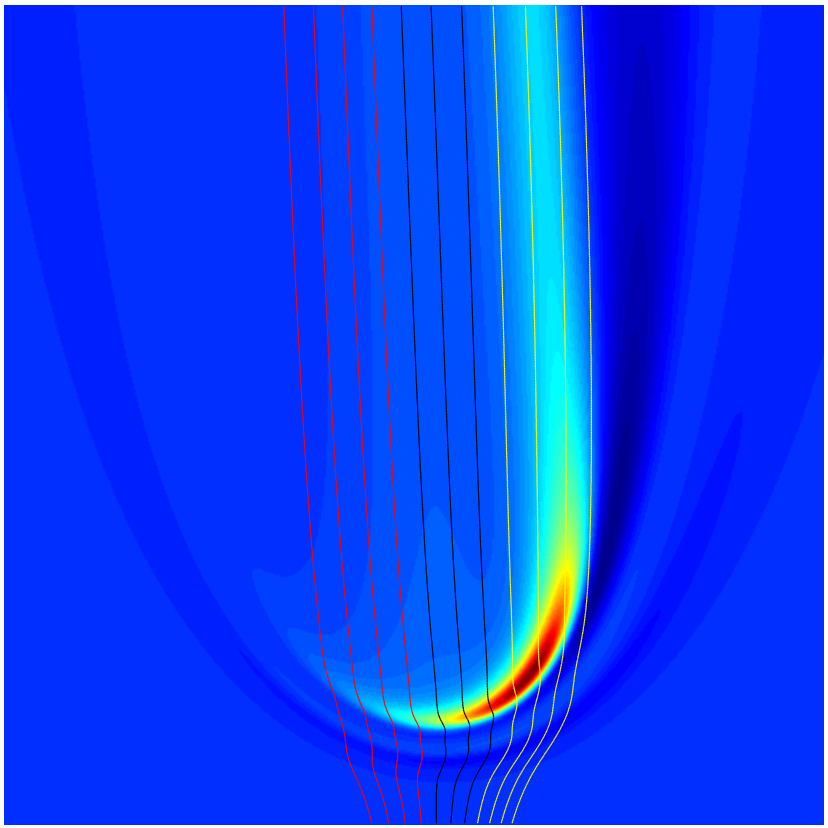
$$HCN \xrightarrow[R231]{+O} NCO \xrightarrow[R223]{+H} NH \xrightarrow[R191]{+H} N \xrightarrow[R180]{+OH} NO$$

- Other NO production/consumption pathways, involving HNO and HNCO, have also been included in the prompt path
- N_2O intermediate pathway
  - $O + N_2 + M \rightarrow N_2O + M$ R185
  - $N_2O + O \rightarrow 2NO$ R182

Edge Flame Structure – NO



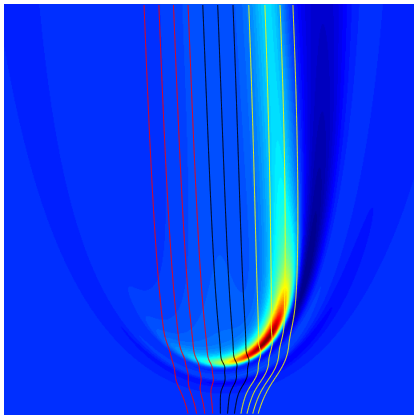
NO



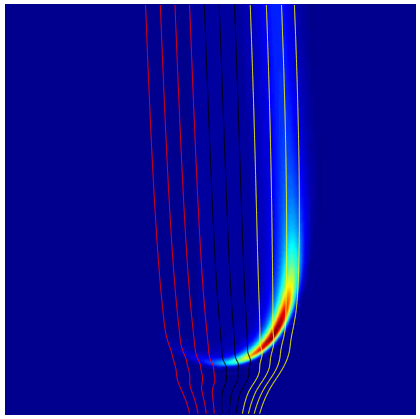
w_{NO}

- Bulk NO production is on the rich side of the edge flame
- Transported to the lean side

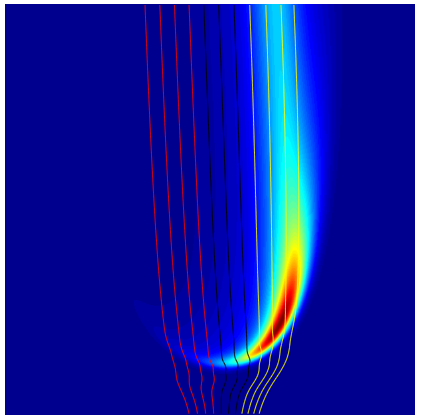
Basic Edge Flame Structure — NO Reactions



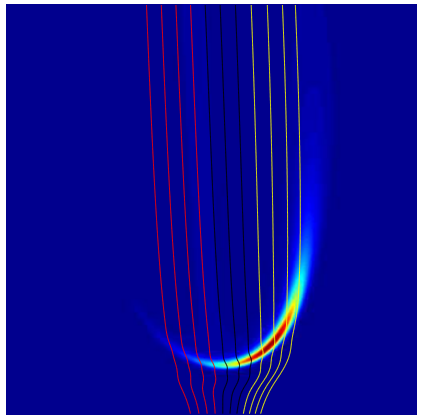
w_{NO}



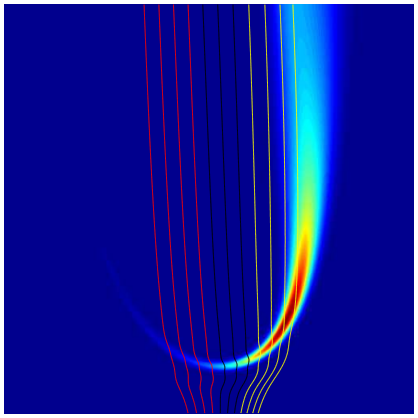
N+OH=NO+H
R180: 1.4×10^{-6}



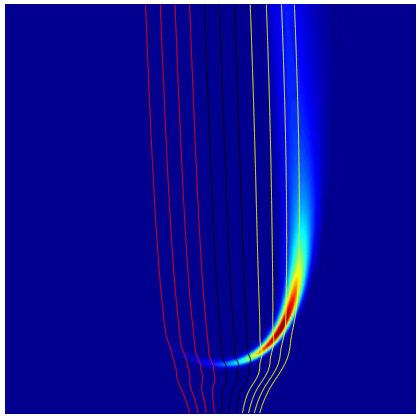
HNO+H=H2+NO
R214: 0.87×10^{-6}



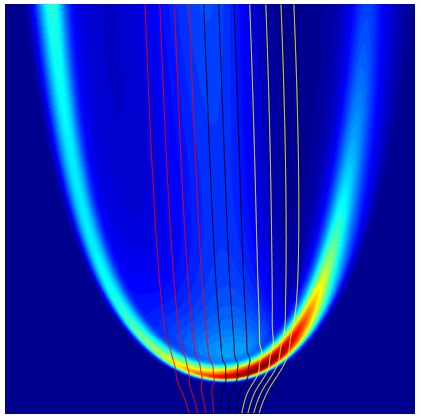
N+O2=NO+O
R179: 0.73×10^{-6}



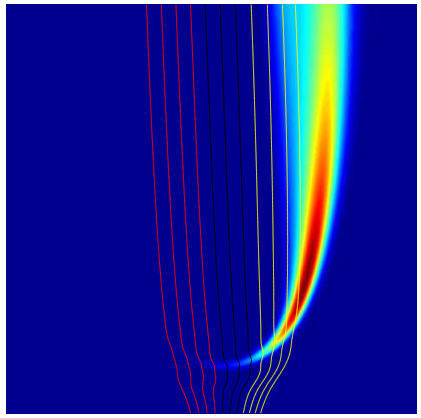
CH2+NO=H+HNCO
R249: 0.43×10^{-6}



CH+NO=HCN+O
R246: 0.32×10^{-6}



NO2+H=NO+OH
R189: 0.32×10^{-6}



HCCO+NO=HCNO+CO
R274: 0.27×10^{-6}

NO Importance Indices — Stoich. Mixture Fraction line ($\xi = 0.055$)

- Cold inflow:

  Convection < 0; Diffusion > 0

- Preheat region:

  Convection < 0; Diffusion > 0

  R189: $NO_2 + H = NO + OH \quad > 0$

  R186: $HO_2 + NO \rightarrow NO_2 + O \quad < 0$

- Premixed front:

  Convection < 0; Diffusion $> / < 0$

  R179: $N{+}O_2 \rightarrow NO{+}O \quad > 0$

  R214: $HNO{+}H \rightarrow H_2{+}NO \quad > 0$

  R249: $CH_2 + NO \rightarrow H + HNCO \quad < 0$

  R223: $NCO + H \rightarrow NH + CO \quad < 0$

  R186: $HO_2 + NO \rightarrow NO_2 + O \quad < 0$

- Trailing Diff flame:

  Convection < 0; Diffusion $\gtrsim 0$

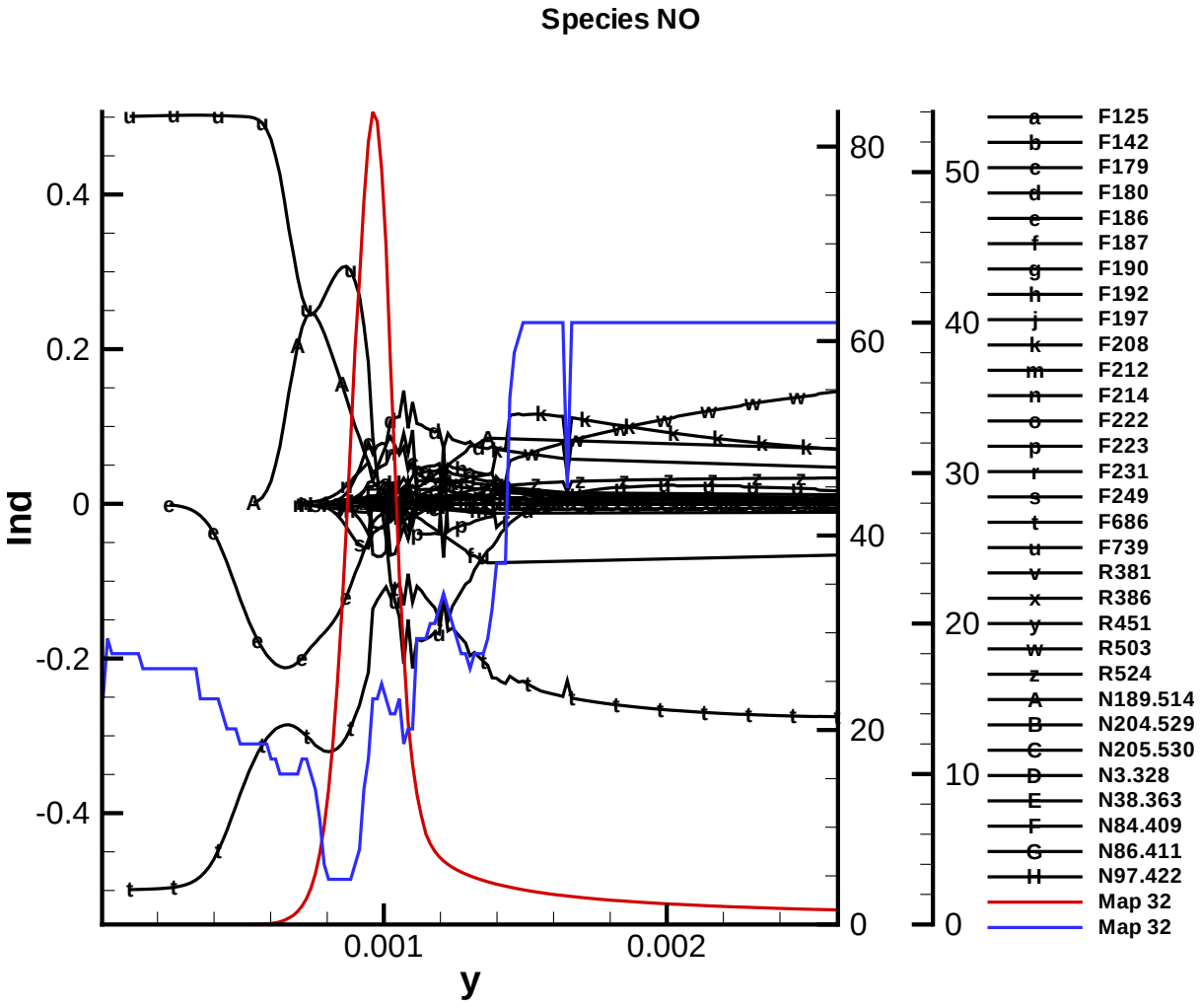
  R178: $N + NO \leftarrow N_2 + O \quad > 0$

  R208: $NNH + O \rightarrow NH + NO \quad > 0$

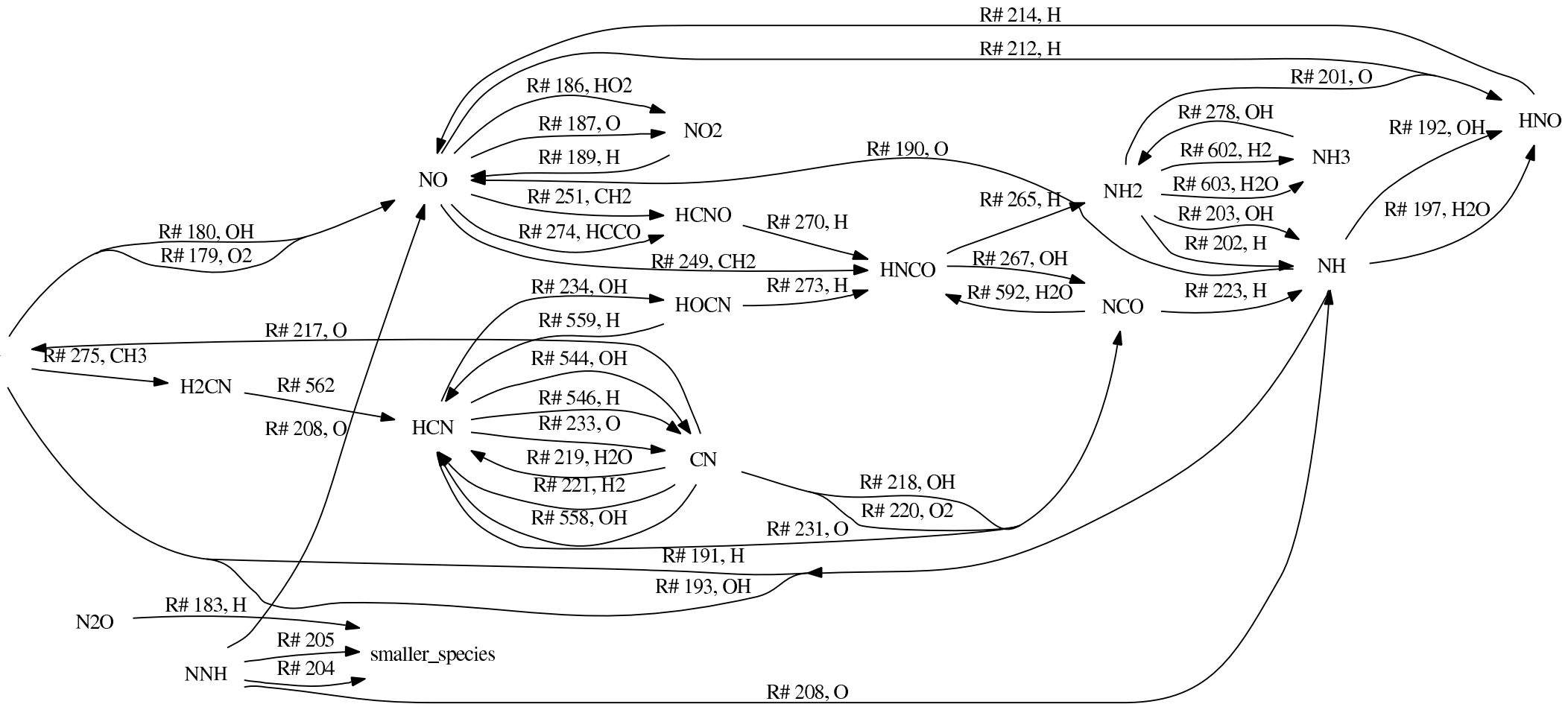
  R189: $NO_2 + H = NO + OH \quad > 0$

  R180: $N + OH \rightarrow NO + H \quad > 0$

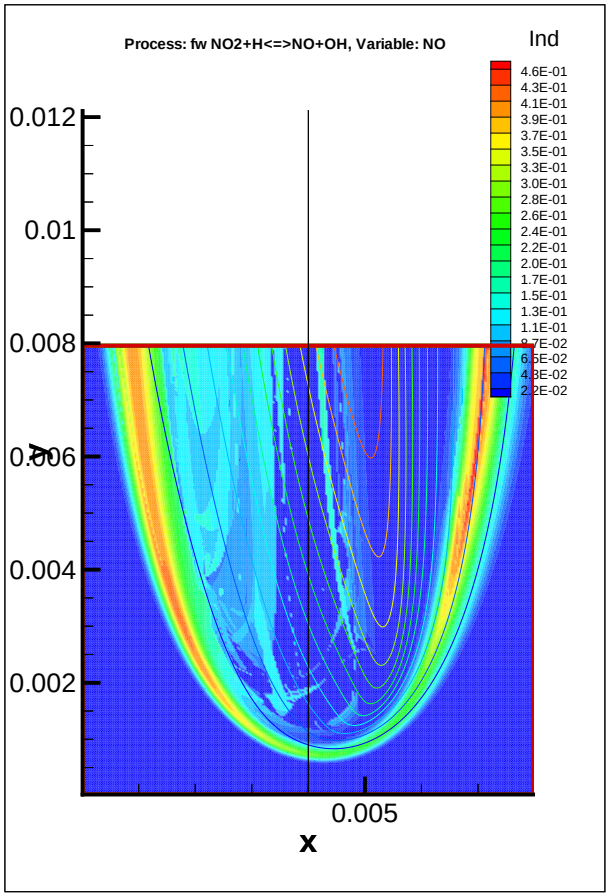
  R187: $NO + O + M \rightarrow NO_2 + M \quad < 0$

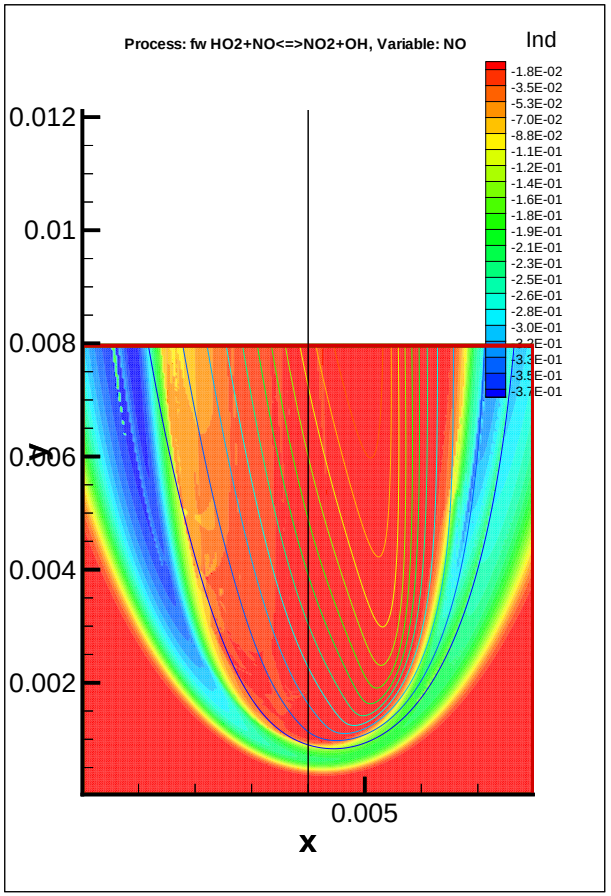


Reaction Graph — Stoich. Mixture Fraction line ($\xi = 0.055$)



Highest NO Importance Indices — Preheat Zone — $\xi \in [0.035, 0.075]$





R189 : $NO_2 + H = NO + OH \quad > 0$

R186 : $HO_2 + NO \rightarrow NO_2 + OH \quad < 0$

with decaying relative influence inside the premixed front

Highest NO Importance Indices — Premixed front

- Rxns with Large $+ve$ Importance, $\xi \in [0.035, 0.075]$:
  R189 : $NO_2 + H = NO + OH$
  R179 : $N + O_2 \rightarrow NO + O$ (Zeldovich)
  R180 : $N + OH \rightarrow NO + H$ (Z)
  R214 : $HNO + H \rightarrow H_2 + NO$ (Prompt)
  - R189 most Imp. +ve for $\xi = \{0.035, 0.075\}$
- Rxns with Large $-ve$ Importance :
  R249 : CH_2+NO $\rightarrow$ H+HNCO $\xi \in [0.045, 0.075]$ (Pr)
  R223 : $NCO + H \rightarrow NH + CO$ ξ_{st} post-flame (Pr)
  R274 : $HCCO + NO \rightarrow HCNO + CO$ $\xi > 0.055$ (Pr)
  R097 : $OH + CH_3 = CH_2(S)$+H_2O $\xi \leq 0.055$

Highest NO Importance Indices — Trailing Diffusion Flame

- Rxns with Large $+ve$ Importance Indices

  R189 : $NO_2 + H = NO + OH \quad \xi \leq \xi_{st}$

  R178 : $N + NO \rightarrow N_2 + O \quad \xi = \xi_{st}$ (Z)

  R208 : $NNH + O \rightarrow NH + NO \quad \xi \in [0.045, \xi_{st}]$

  R180 : $N + OH \rightarrow NO + H \quad \xi \in [\xi_{st}, 0.065]$ (Pr)

  R197 : $NH + H_2O \rightarrow HNO + H_2 \quad \xi = 0.065$

  R214 : $HNO + H \rightarrow H_2 + NO \quad \xi = 0.075$ (Pr)

- Rxns with Large $-ve$ Importance Indices

  R187 : $NO + O + M = NO_2 + M \quad \xi \in [0.035, \xi_{st}]$

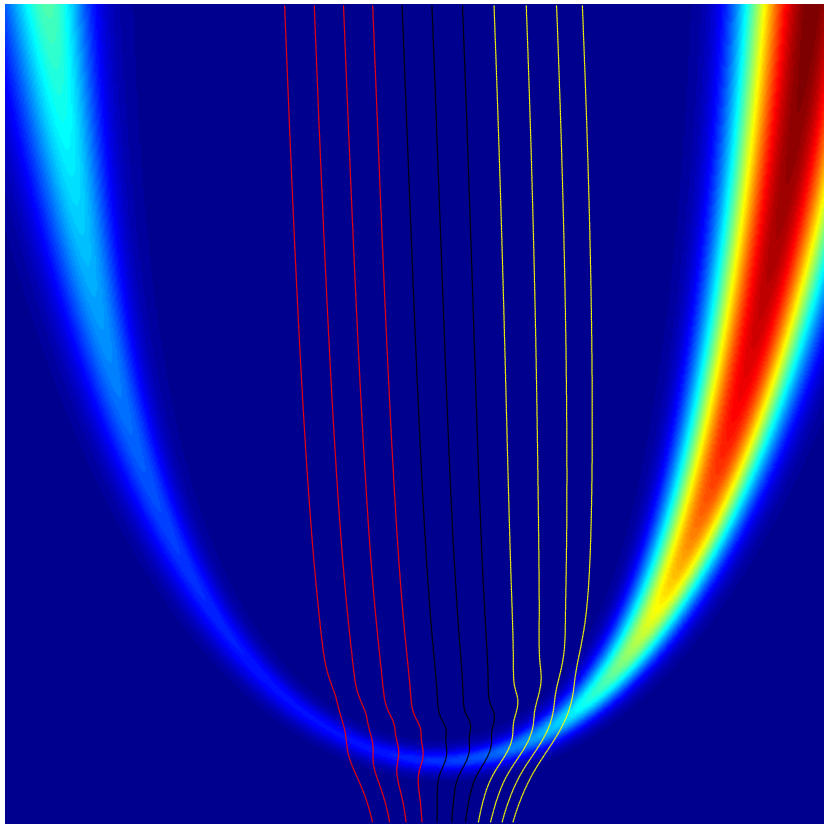
  R192 : $NH + OH \rightarrow HNO + H \quad \xi = 0.065$

  R223 : $NCO + H \rightarrow NH + CO \quad \xi = 0.065$ (Pr)

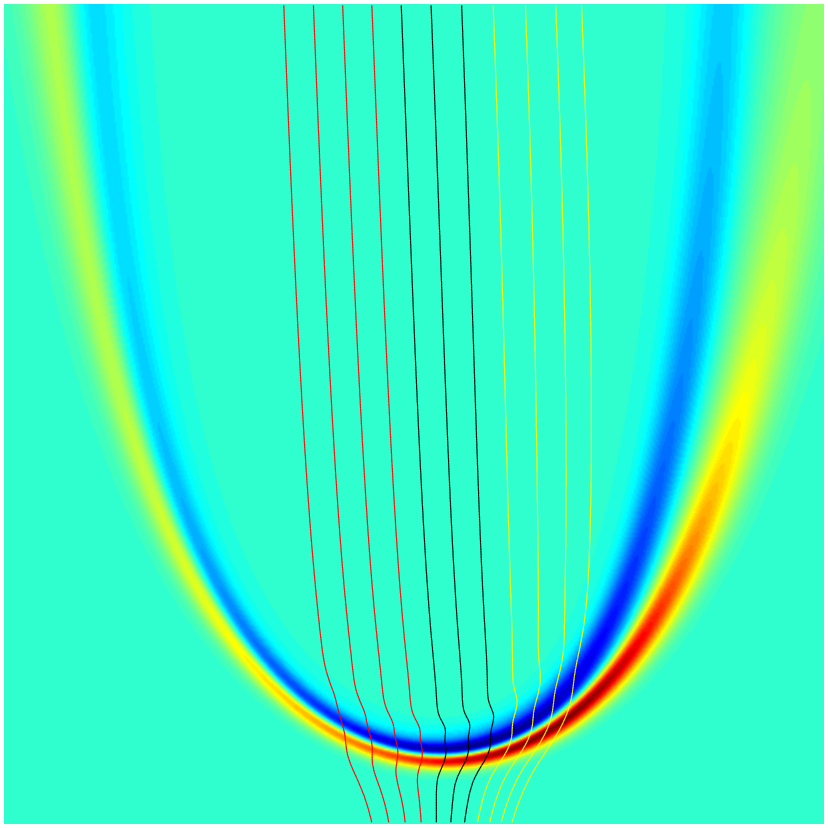
  R274 : $HCCO + NO \rightarrow HCNO + CO \quad \xi = 0.075$ (Pr)

  R249 : $CH_2 + NO \rightarrow H + HNCO \quad \xi = 0.075$ (Pr)

Edge Flame Structure – NO_2



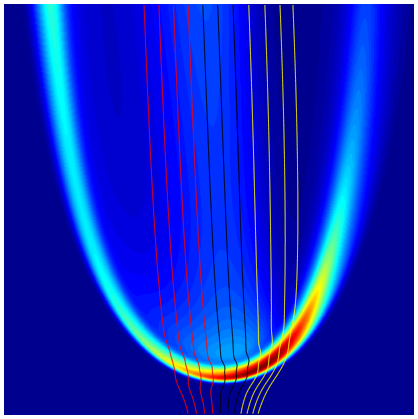
NO_2

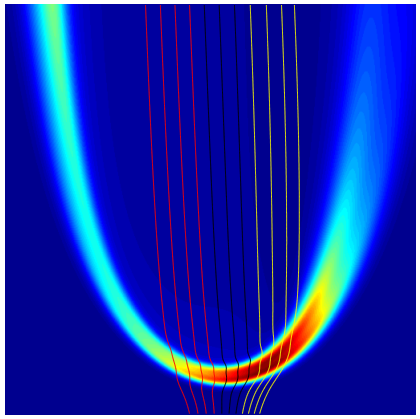


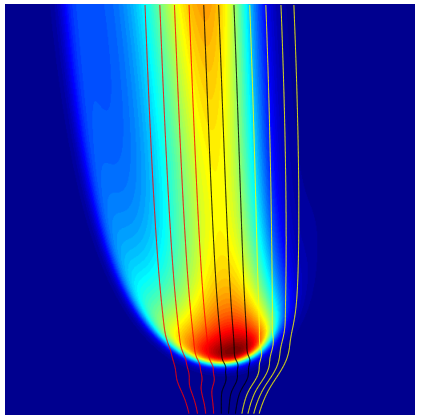
w_{NO_2}

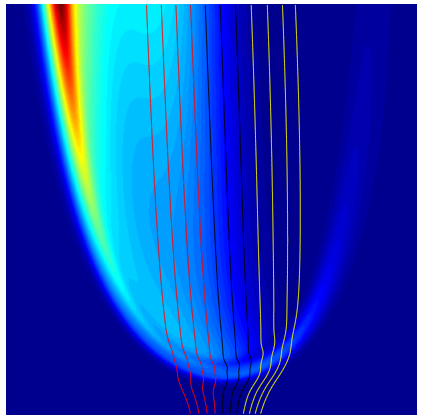
- NO_2 is a component of NOx

Basic Edge Flame Structure — NO_2 Reactions


NO_2+H=NO+OH
R189: 3.2×10^{-7}

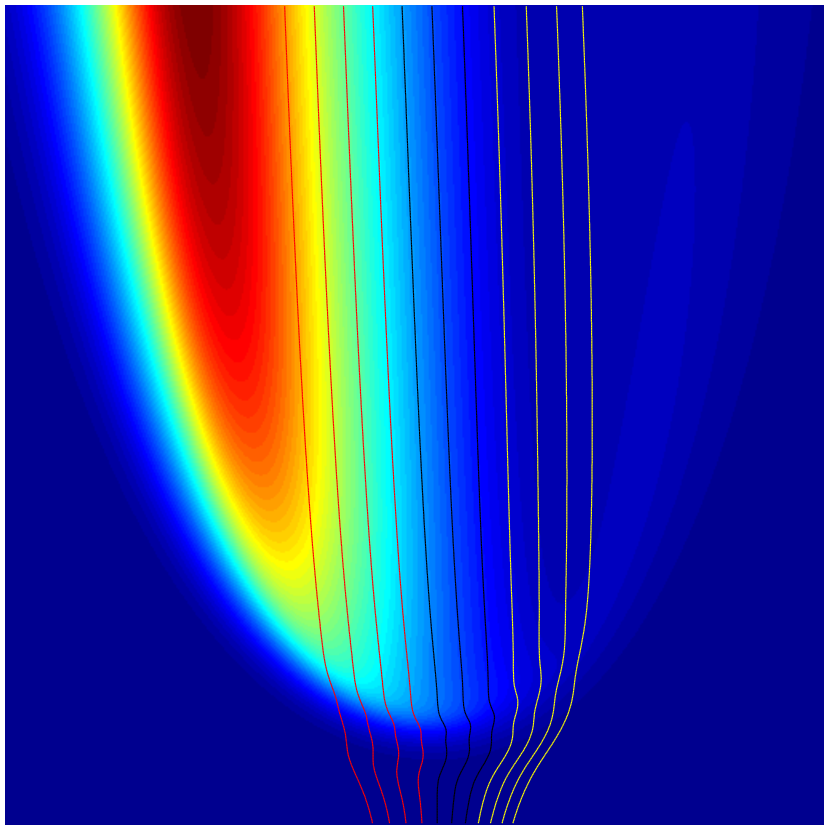

HO_2+NO=NO_2+OH
R186: 2.4×10^{-7}


NO+O+M=NO_2+M
Rl87: 0.78×10^{-7}

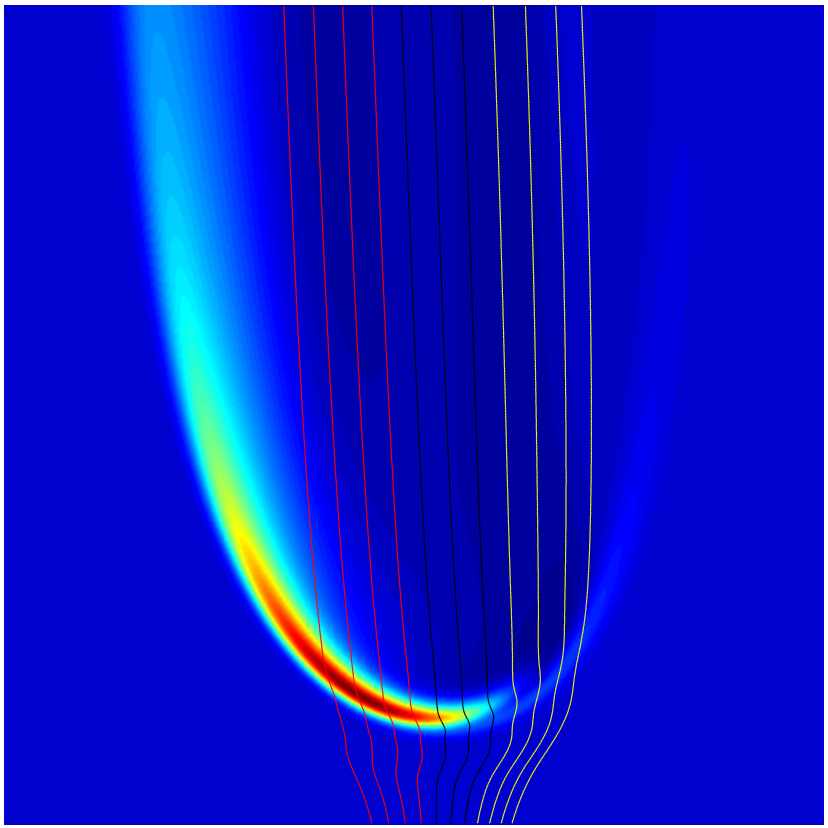

NO_2+O=NO+O_2
Rl88: 0.08×10^{-7}

- Reactions with Large positive Importance to NO_2
  - R186 : HO_2+NO=NO_2+OH all ξ ($\rightarrow$ for $\xi = 0.075$)
  - R187 : NO+O+M=NO_2+M $\xi \in [0.035, \xi_{st}]$
- Reactions with Large negative Importance to NO2
  - R189 : NO_2+H=NO+OH all ξ

Edge Flame Structure – N_2O



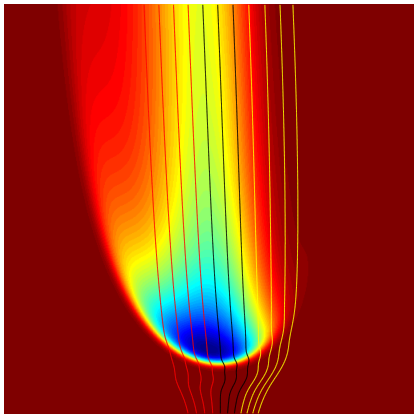
N_2O



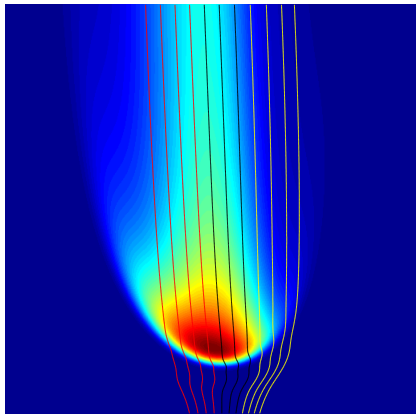
w_{N_2O}

- N_2O is a greenhouse gas
- Important intermediate for NO production

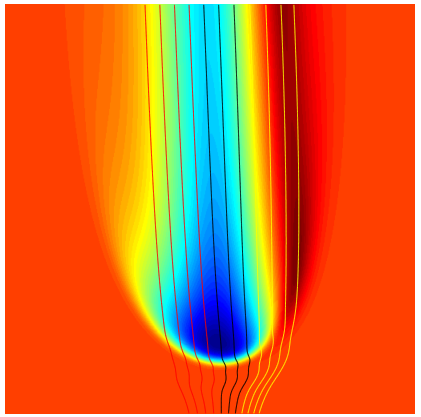
Basic Edge Flame Structure — N_2O Reactions



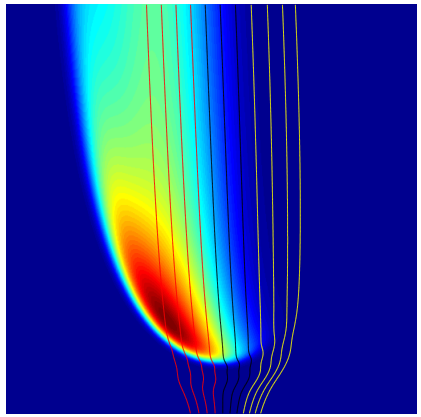
$N_2O(+M)=N_2+O(+M)$
R185: 8.5×10^{-8}



$N_2O+H=N_2+OH$
R183: 7.0×10^{-8}



$NH+NO=N_2O+H$
R199: 1.1×10^{-8}



$N_2O+O=N_2+O_2$
R181: 0.2×10^{-8}

- Reactions with Large positive Importance to N_2O
  - R185 : $N_2O(+M)=N_2+O(+M)$ all ξ (prem for $\xi = 0.075$)
  - R199 : $NH+NO=N_2O+H$ $\xi = 0.075$ ($\lesssim 0$ for $\xi = \xi_{st}$)
  - R184 : $N_2O+OH \leftarrow N_2+HO_2$ $\xi = 0.075$ (prem)
  - R038 : $H+O_2 \rightarrow O+OH$ $\xi = 0.075$ (diff)
- Reactions with Large negative Importance to N_2O
  - R183 : $N_2O+H=N_2+OH$ all ξ ($\rightarrow$ for $\xi = 0.075$)

Conclusions

- Analyzed dynamical structure of hydrocarbon and nitrogen chemistry in a methane-air edge flame
  - Manifold structure, time scales, importance indices
- Large number of modes exhausted behind the premixed flame front
- Larger separation between low-T and primary reactive layers on the rich side of the edge flame
  - Slower low-T active process on the rich side
- Identified important NO, N_2O, and NO_2 reactions in different regions of the edge flame
  - Significant contributions by various NOx pathways
    - Zeldovich, Prompt, NNH
  - Strong role for NO_2-mediated NO production/consumption