High-Pressure Kinetic Mechanisms for Hydrogen and Hydrogen Syngas

1st International Workshop on Flame Chemistry
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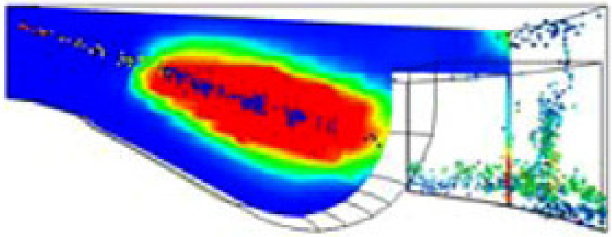
Stephen Klippenstein, Lawrence Harding

Motivation

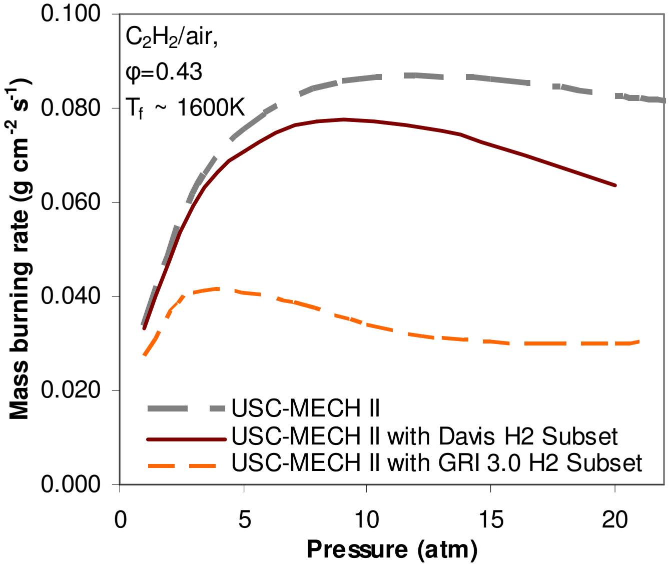
- Growing interest in computational engine design/testing
    - Fluid mechanics and kinetics sub-models



(Shi & Reitz 2010)

- H_2 and H_2/CO
    - Synthesis gas ($H_2/CO/H_2O/CO_2$) from coal/biomass gasification
    - Core sub-model for all fuels

- Advanced engine technologies → High P, low T_f
    - Modeling difficulties for flames



(Burke et al. 2011)

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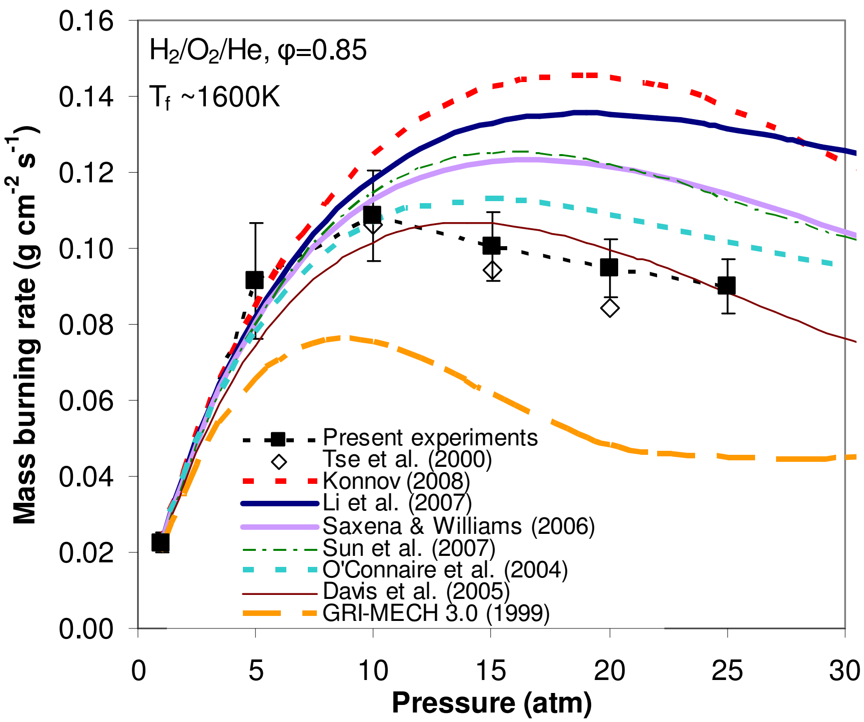
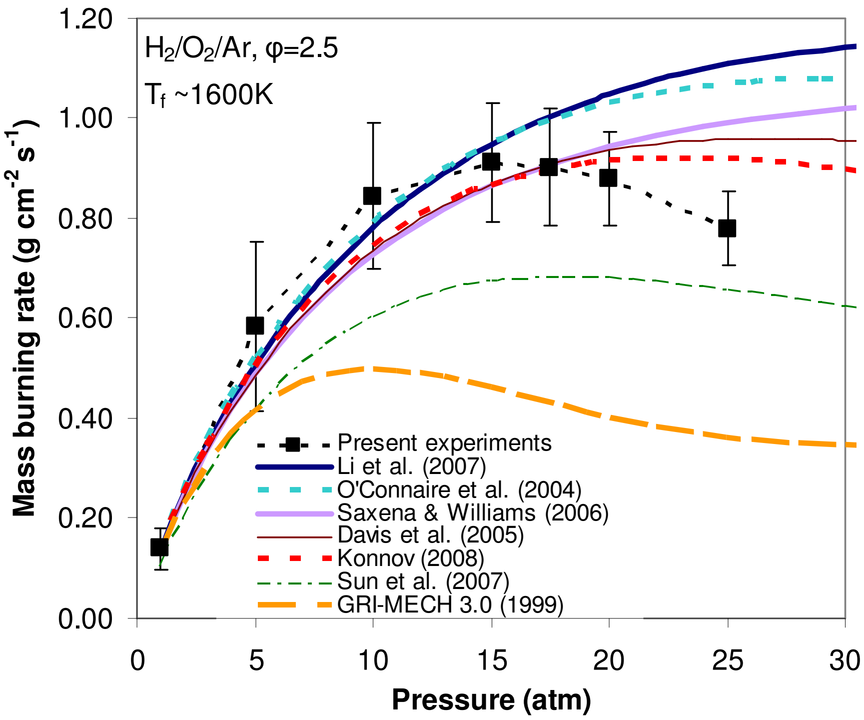
1. Y. Shi, R.D. Reitz, Fuel 89 (2010) 3416–3430.
2. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, Combustion and Flame 157 (2010) 618-631.
3. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Difficulty in predicting high-pressure flames





- Large variations among models
- None of the models capture pressure dependence across all conditions

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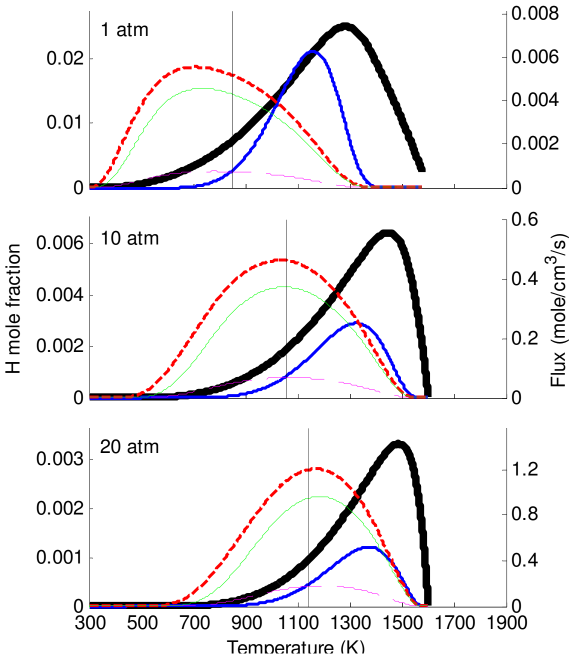
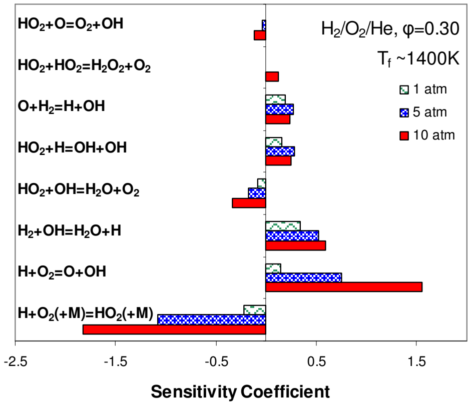
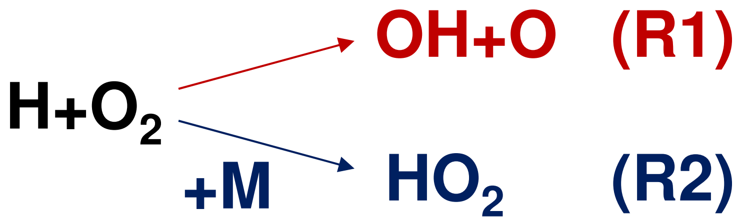
1. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, *Combustion and Flame* 157 (2010) 618-631.
2. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

What controls high-P/low-T_f flames?







increasing P

- More HO_2
  - → *more HO_2+radical flux*
- Flame zone shifts
  - → *peak sensitivity at higher T's*
  - → *collision efficiencies of products*
- More R1/R2 competition
  - → *amplified sensitivity*

(Situation similar for H_2/CO)

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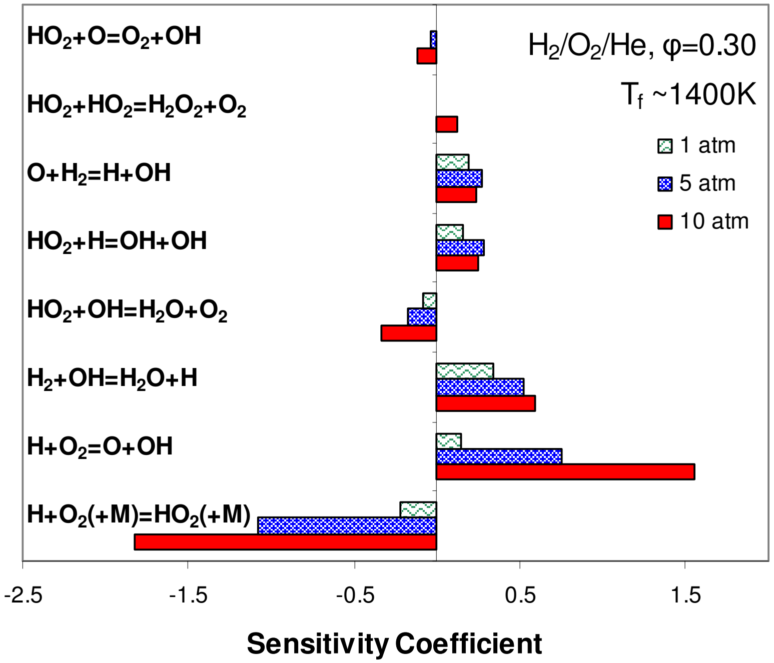
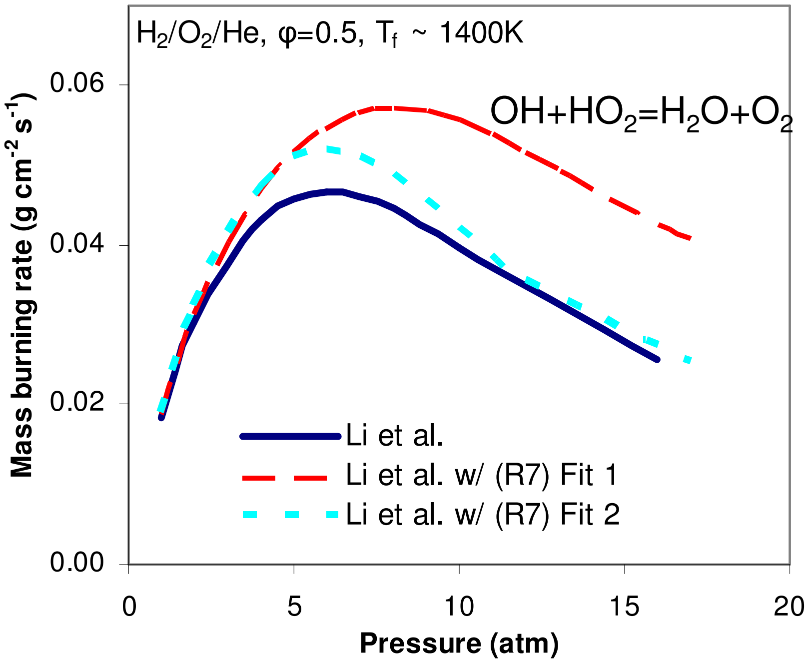
1. M.P. Burke, M. Chaos, F.L. Dryer, Y. Ju, *Combustion and Flame* 157 (2010) 618-631.
2. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Complexity of the modeling problem





- Uncertainty in all reactions of 10% →burning rate uncertainty of 30%
- Realistic accuracy improvements for *elementary reactions* will not yield typical expected accuracies for *global behavior*
- Optimization against global targets necessary

- Functional temperature dependence of OH+HO_2=H_2O+O_2 highly disputed/ unknown
- Parameter optimization techniques don't work if the *functional dependence* is not known

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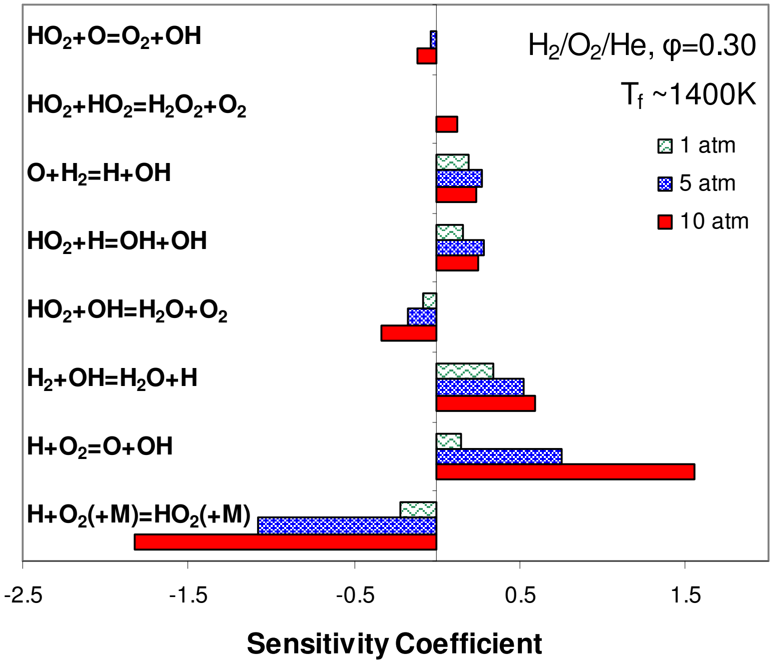

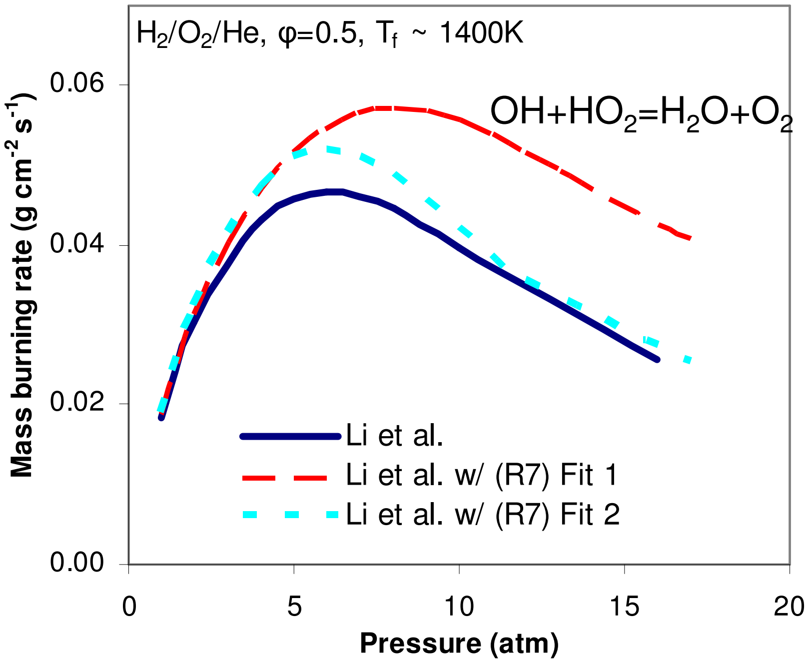

- A rigorous modeling solution will likely require ***<u>both</u>***:
  - Empirical adjustments to rate constants
  - Improved fundamental understanding of select processes
- Neither alone appears sufficient to solve the problem.

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1. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Updated kinetic-transport models

- H_2: Hong et al. (2011) and Burke et al. (2012)*
  - HO_2 formation/consumption
    - $H+O_2(+M) = HO_2(+M)$
    - HO_2+radical reactions
  - H_2O_2 reactions
  - … among others

- CO: Haas et al. (2012)
  - $CO + OH = CO_2 + H$, $CO + HO_2 = CO_2 + OH$
  - HCO chemistry

* *Uncertainties remained: adjustments of rate parameters to improve predictions*

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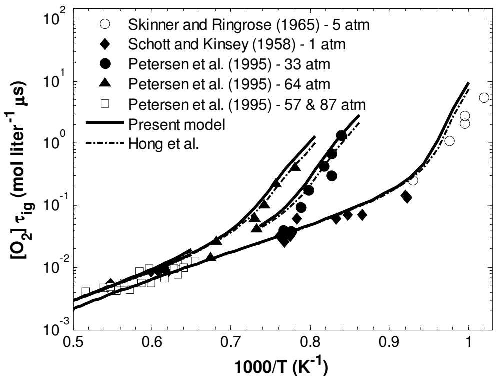
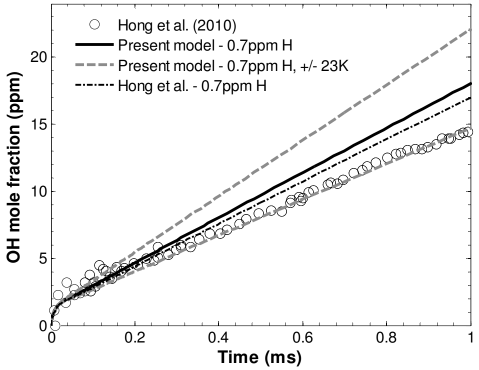
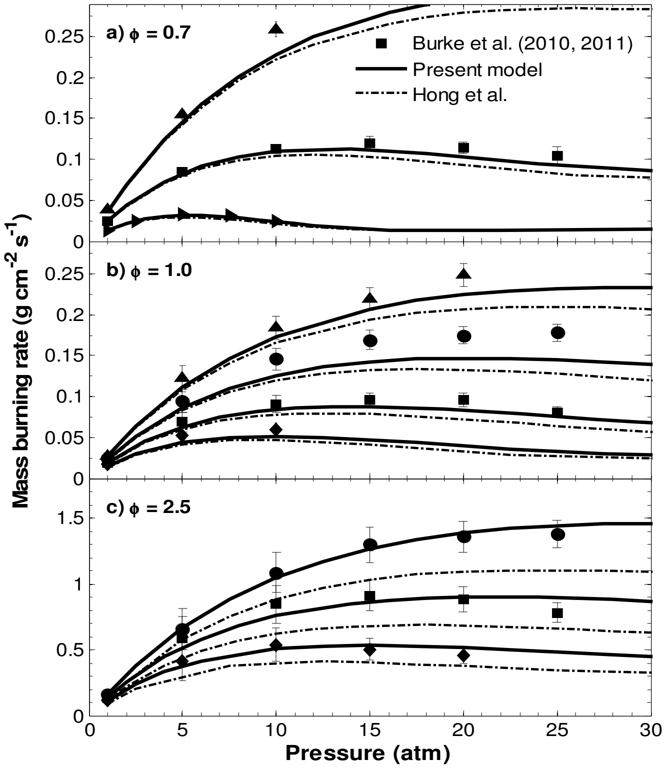
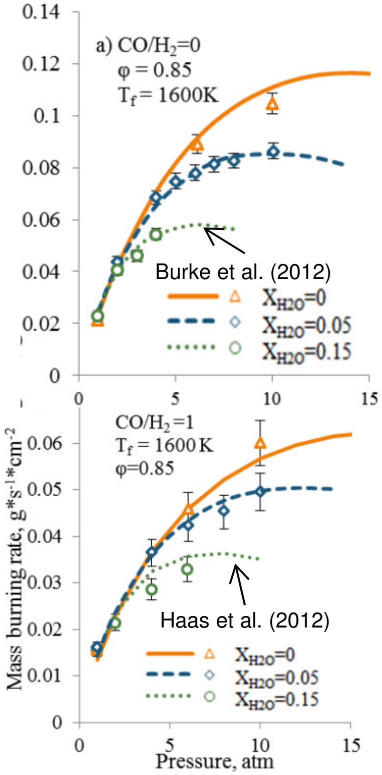
1. Z. Hong, D.F. Davidson, R.K. Hanson, *Combust. Flame* 158 (2011) 633–644.
2. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
3. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.

Model performance









(Santer et al. 2012, 5E01 on Friday)

- Hong/Burke perform similarly well against most targets
- Largest differences in flames
  - Burke et al. – within 20%, Hong et al. – within 40%
- Parameter adjustments not unique → uncertainties remain!

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1. Z. Hong, D.F. Davidson, R.K. Hanson, *Combust. Flame* 158 (2011) 633–644.
2. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
3. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.
4. J. Santner, F.L. Dryer, Y. Ju, *Proc. Combust. Inst.* (2012) in press, oral presentation : 5E01 on Friday.

Uncertainties remaining in 2012 (for flames)

- Parametric uncertainties
  - $HO_2 + X$ reactions
    - $HO_2 + H = OH + OH$
      $H_2 + O_2$
      $H_2O + O$
    - ***$HO_2 + OH = H_2O + O_2$***
    - $HO_2 + HO_2 = H_2O_2 + O_2$
  - $H + O_2 (+M) = HO_2 (+M)$
    - Pressure dependence
    - 3rd body efficiencies for H_2O and *CO_2*
  - $CO + O + M = CO_2 + M$
- Model assumptions
  - Nonlinear mixture rules

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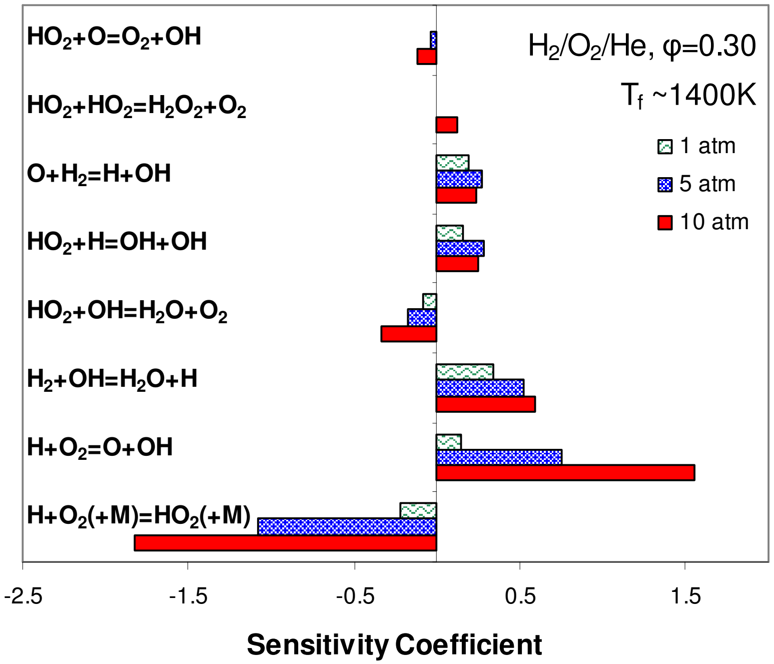
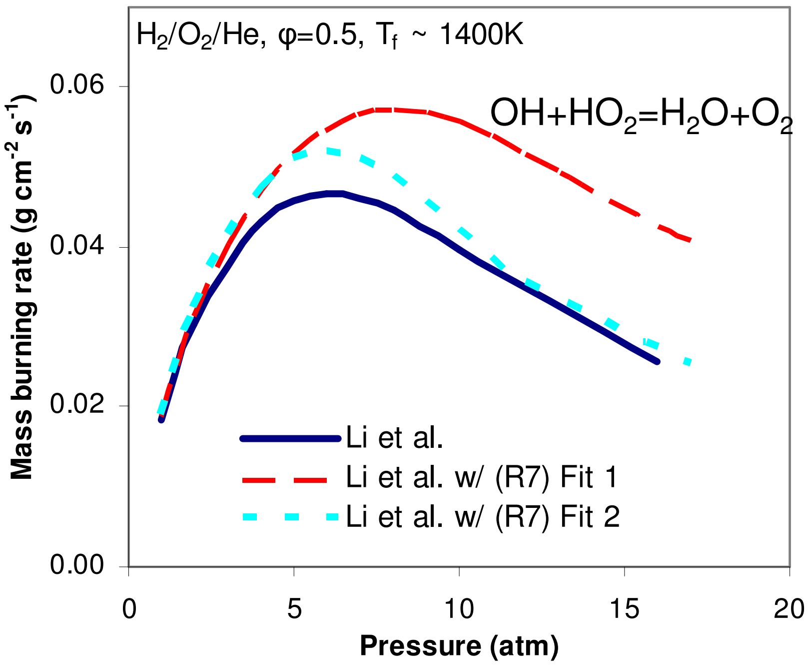
1. M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, *Int. J. Chem. Kinet.* 44 (2012) 444-474.
2. F.M. Haas, S. Vranckx, M. Chaos, R.X. Fernandes, F.L. Dryer (2012) in preparation.
3. P. Saxena, F.A. Williams, 7th US National Combustion Meeting, Atlanta, GA , 2011.

Recall the complexity of the modeling problem and uncertainties in $OH+HO_2 = H_2O+O_2$





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1. M.P. Burke, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* 33 (2011) 905-912.

Modeling strategies

- **Current kinetic models: <u>sets of rate parameters</u>**
  - Hierarchical, comprehensive modeling
    - Westbrook & Dryer (1984)
  - Optimization and Uncertainty Quantification
    - Frenklach (1984), Frenklach,Wang,Rabinowitz (1992):Solution-mapping + optimization of *A*-factors
    - Frenklach et al. (2004), Sheen & Wang (2009): Uncertainty Quantification of *A*-factors
    - Turányi et al. (2012), Sheen et al. (2012): Uncertainty quantification of A-n-E_a
  - Require massive amounts of data to constrain full *T*/*P*/*M*-dependence of all *k*'s
    - Extrapolation outside the dataset very challenging
- Direct incorporation of theory useful
  - Replaces fitting formulas with physical theories
  - Common for extrapolation of data for a single reaction
  - Imposes constraints spanning all *T*/*P*/*M*
- ***Multi-scale models: <u>sets of molecular parameters</u>***
  - Optimal use of information from *ab initio* calculations, *k* measurements, combustion measurements
  - Theory *fills in the gaps* across all *T*/*P*/*M*

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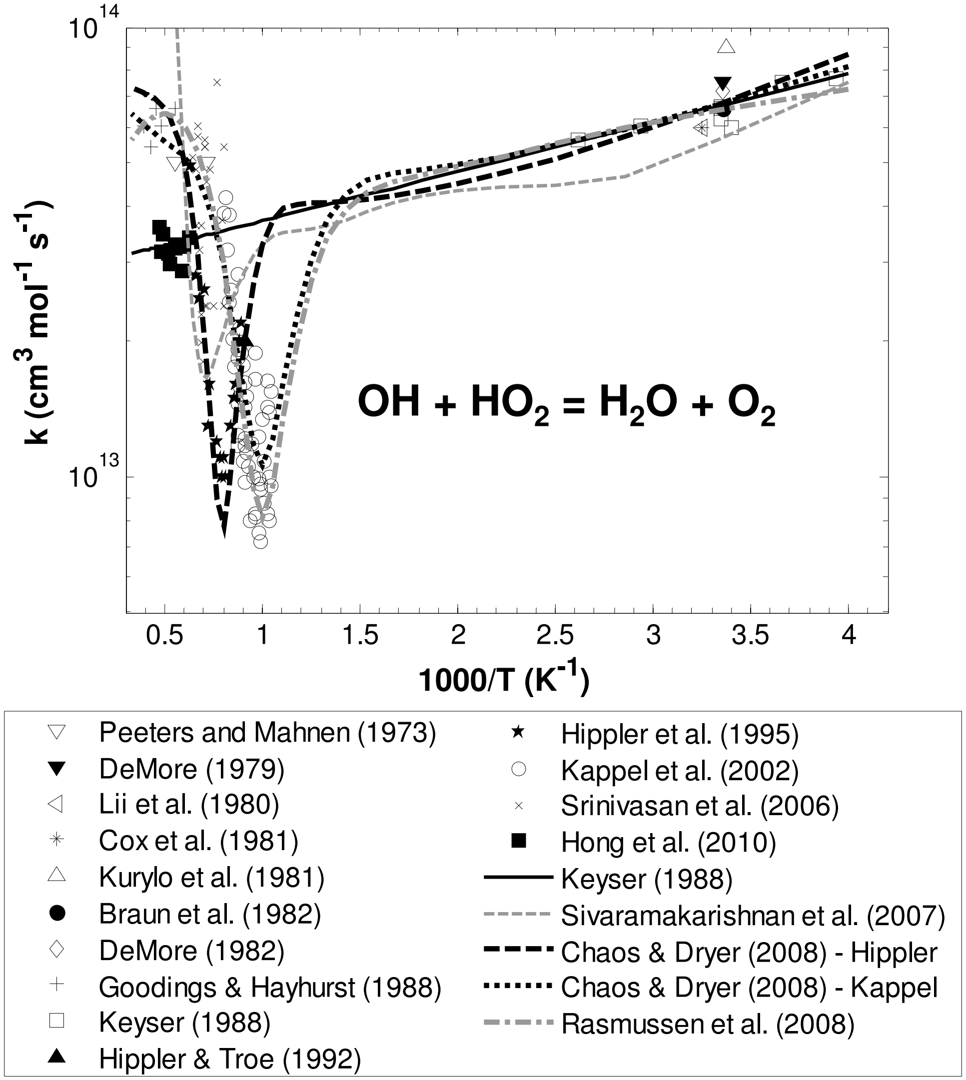
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

$OH + HO_2 = H_2O + O_2$



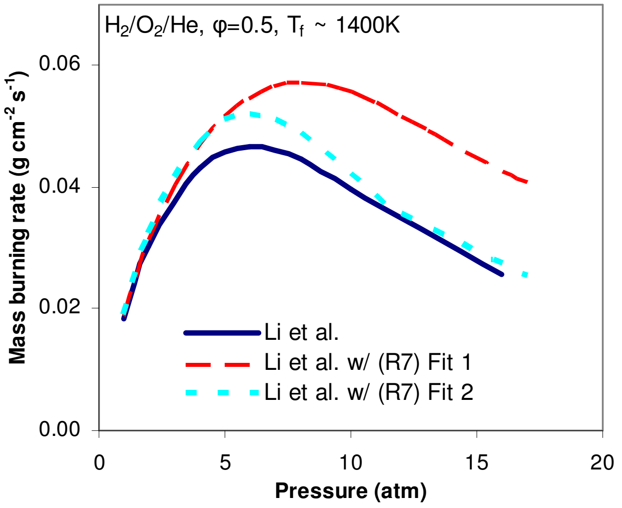
(R1) $H_2O_2(+M) = OH+OH(+M)$

(R2) $H_2O_2+OH = HO_2+H_2O$

(R3) $HO_2+HO_2 = H_2O_2+O_2$

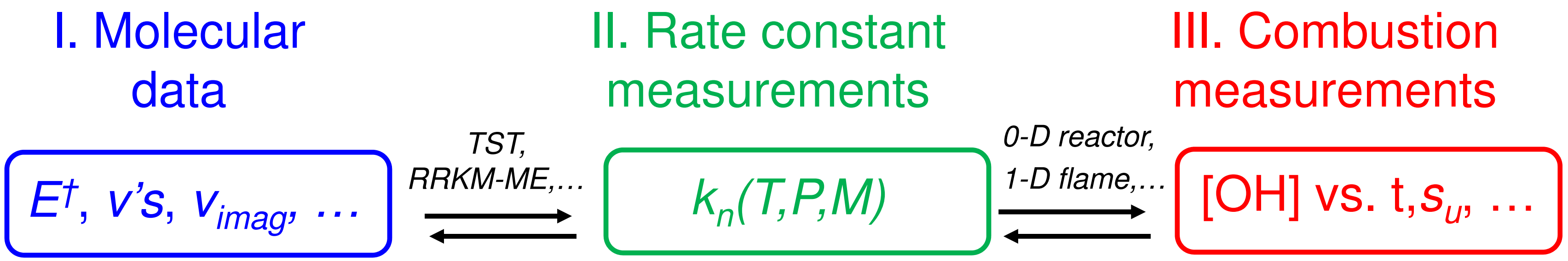
(R4) $HO_2+OH = H_2O+O_2$

(R5) $OH+OH = O+H_2O$



Multi-scale informatics

***set of molecular parameters* informed by data across all scales**



I. Molecular data

II. Rate constant measurements

III. Combustion measurements

$E^\dagger$, ν's, ν_{imag}, …

TST, RRKM-ME,…

$k_n(T,P,M)$

0-D reactor, 1-D flame,…

[OH] vs. t, s_u, …

Mathematical implementation

- Local “surrogate model”
- Least-squares error minimization
- Iterated until converged

X = Optimization parameters:

Molecular parameters + experimental conditions

$E^\dagger$, ν's, ν_{imag}, … + T, P, $[M_i]$,…

$$F_i(X_j) = Y_{t,i} \pm Z_i$$

(I) + (IV) $\Rightarrow$ $S_{ij} = \delta_{ij}$

(II) $\rightarrow$ $S_{ij} = \dfrac{\partial \ln k_{p,n}(T_i, P_i, M_i)}{\partial X_j}$

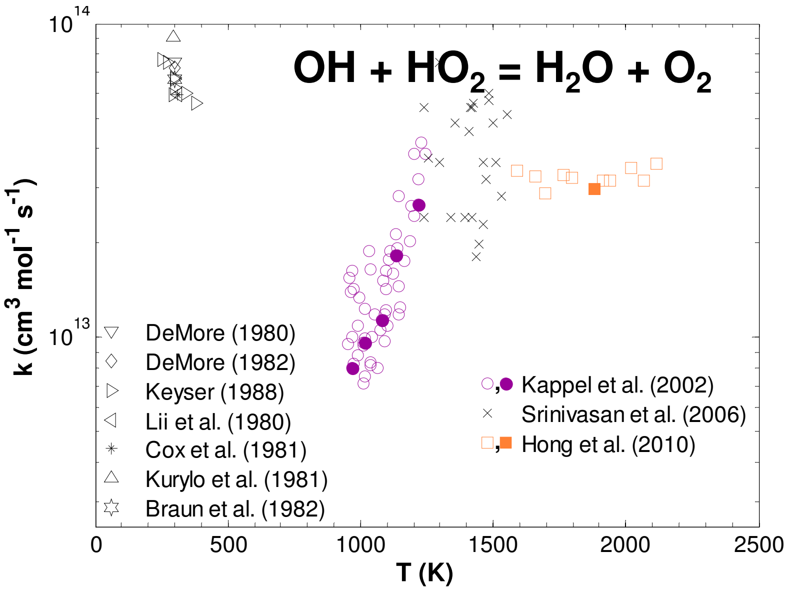
(III) $\rightarrow$ $S_{ij} = \sum_n \dfrac{\partial F_i}{\partial \ln k_{p,n}(T_i, P_i, M_i)} \dfrac{\partial \ln k_{p,n}(T_i, P_i, M_i)}{\partial X_j}$

$$\sum_j S_{ij}(X_j - \tilde{X}_j) = Y_i \pm Z_i \longrightarrow \boxed{X_{j,opt} \text{ and } C_X}$$

Implementation for H_2O_2 system

Optimization variables

$H_2O_2(+M) = OH+OH(+M)$	$A'_{(1)}, n_{(1)}, E_{(1)}$
$H_2O_2+OH = HO_2+H_2O$	$E^{\dagger}_{(2)}, \nu'_{all(2)}, \nu'_{tr(2)}, \nu'_{ss(2)}, \nu'_{imag(2)}, E_{w(2)}, \eta'_{H2O2}, \eta'_{TS(2)}$
$HO_2+HO_2 = H_2O_2+O_2$	$E^{\dagger}_{(3)}, \nu'_{all(3)}, \nu'_{tr(3)}, \nu'_{ss(3)}, \nu'_{imag(3)}, E_{w(3)}, \eta'_{TS(3)}$
$HO_2+OH = H_2O+O_2$	$E^{\dagger}_{(4g)}, \nu'_{all(4)}, \nu'_{tr(4g)}, \nu'_{ss(4g)}, \nu'_{imag(4g)}, E_{w(4g)}, \eta'_{TS(4g)}$
	$E^{\dagger}_{(4e)}, \nu'_{TS(4e)}, \nu'_{tr(4e)}, \nu'_{ss(4e)}, \eta'_{TS(4e)}, f'_{VRCTST,c(4)}$
$OH+OH = O+H_2O$	$E^{\dagger}_{(5g)}, \nu'_{all(5)}, \nu'_{tr(5g)}, \nu'_{ss(5g)}, \nu'_{imag(5g)}, E_{w(5g)}$
	$E^{\dagger}_{(5e)}, \nu'_{TS(5e)}, \nu'_{tr(5e)}, \nu'_{ss(5e)}$
Shock-heated $H_2O_2/H_2O/O_2/Ar$	$T'_i, P'_i, M'_{H2O2,o,i}, M'_{H2O,o,i}, M'_{O2,o,i}$
Shock-heated $H_2O/O_2/Ar$	$T'_i, P'_i, M'_{H2O,o,i}, M'_{O2,o,i}, M'_{H,o,i}$
Shock-heated H_2O_2/Ar	$T'_i, P'_i, M'_{H2O2,o,i}, \sigma'_{1,H2O2}, \sigma'_{2,H2O2}, \sigma'_{1,HO2}, \sigma'_{2,HO2}$



Optimization Targets

I. Molecular data:

ab initio calculations (Klippenstein/Harding)

II. Rate constant measurements:

see paper

III. Combustion measurements:

OH(t), H_2O(t)	*Shock-heated H_2O_2/Ar (Hong et al. 2009,2010)*
OH(t)	*Shock-heated H_2O/O_2/Ar (Hong et al. 2010)*
abs_{215nm}(t)	*Shock-heated H_2O_2/Ar (Kappel et al. 2002)*

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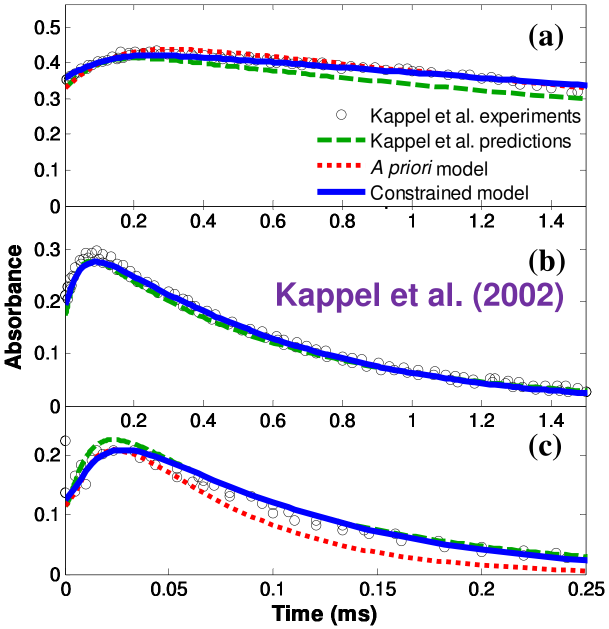
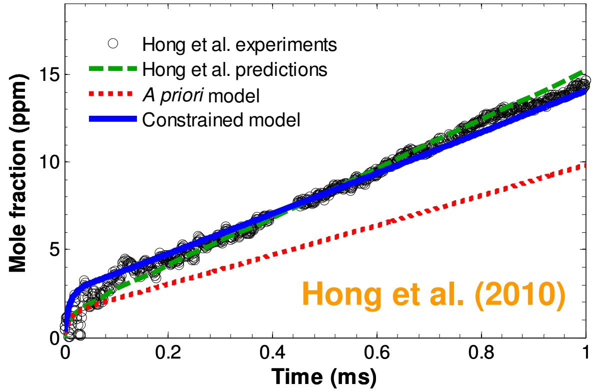
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Different interpretations for $OH+HO_2$



Much weaker *T*-dependence

(Secondary reactions)



Lower magnitude

(Arbitrary H atom doping)

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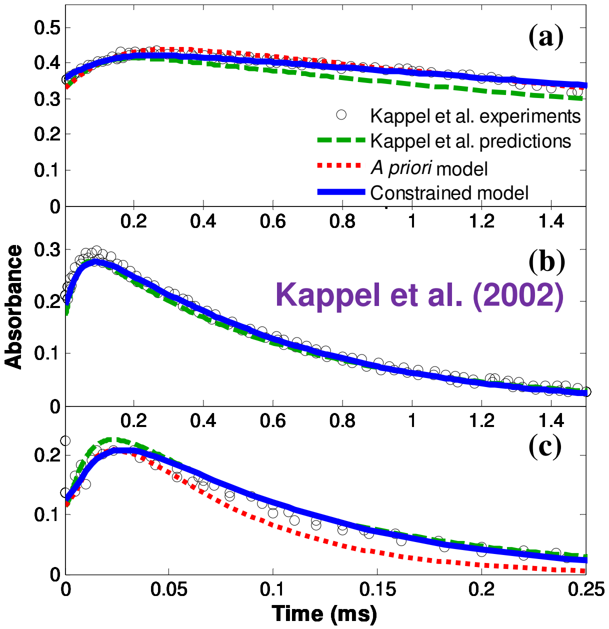
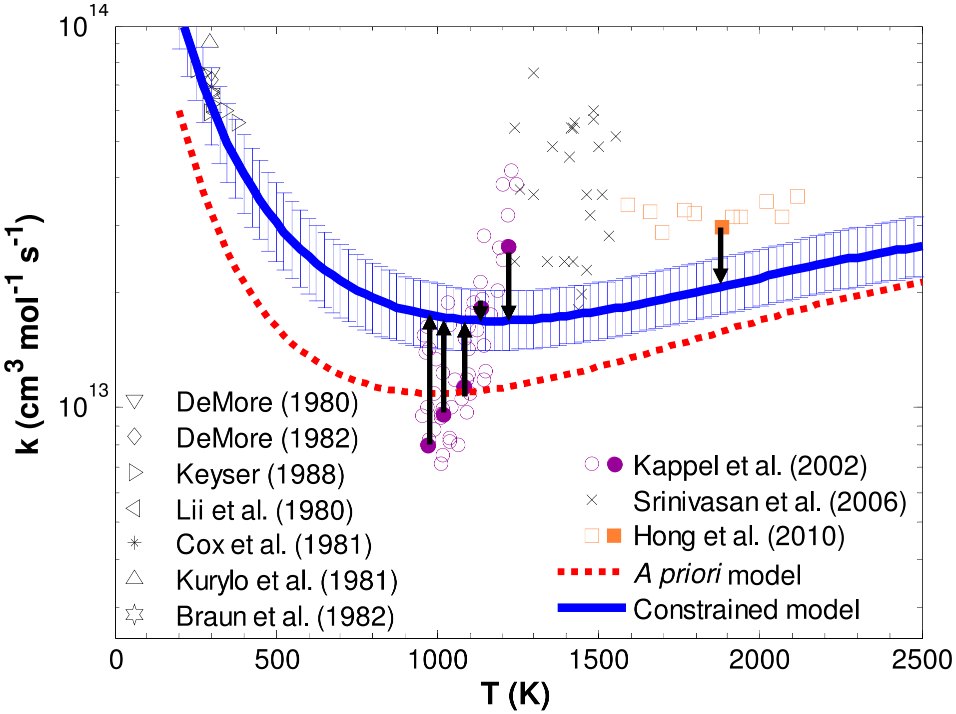
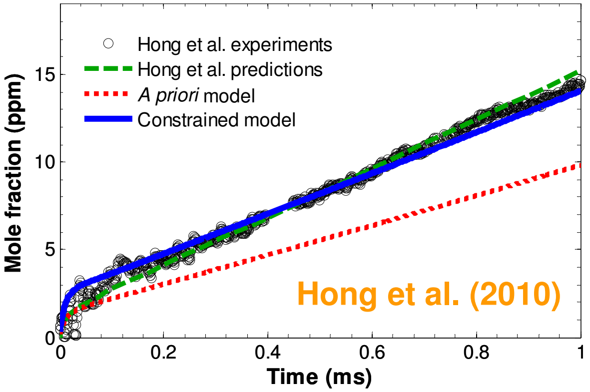
1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

Consistent description of $OH+HO_2 = H_2O+O_2$







- Single description consistent with:
  1. *Ab initio* calculations
  2. Low-*T* *k* measurements
  3. High-*T* raw global data
- Milder *T*-dependence
  - Minimum near 1200 K

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1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.

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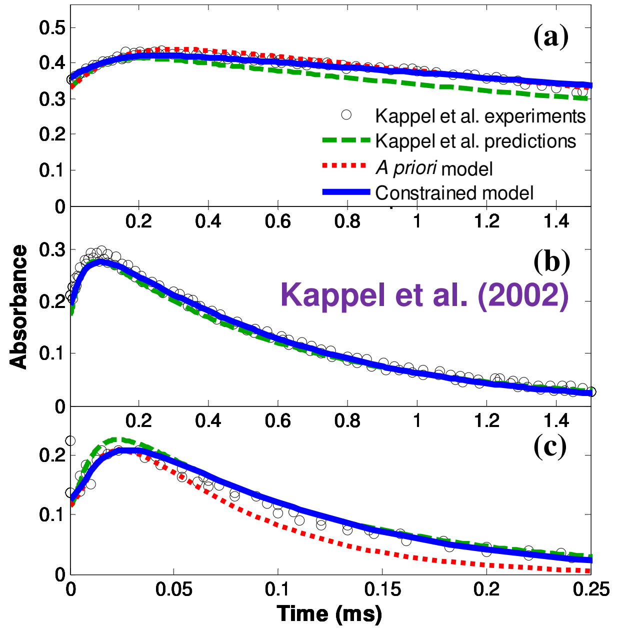

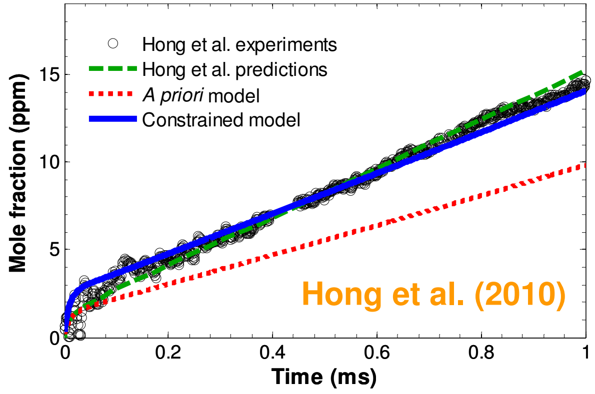

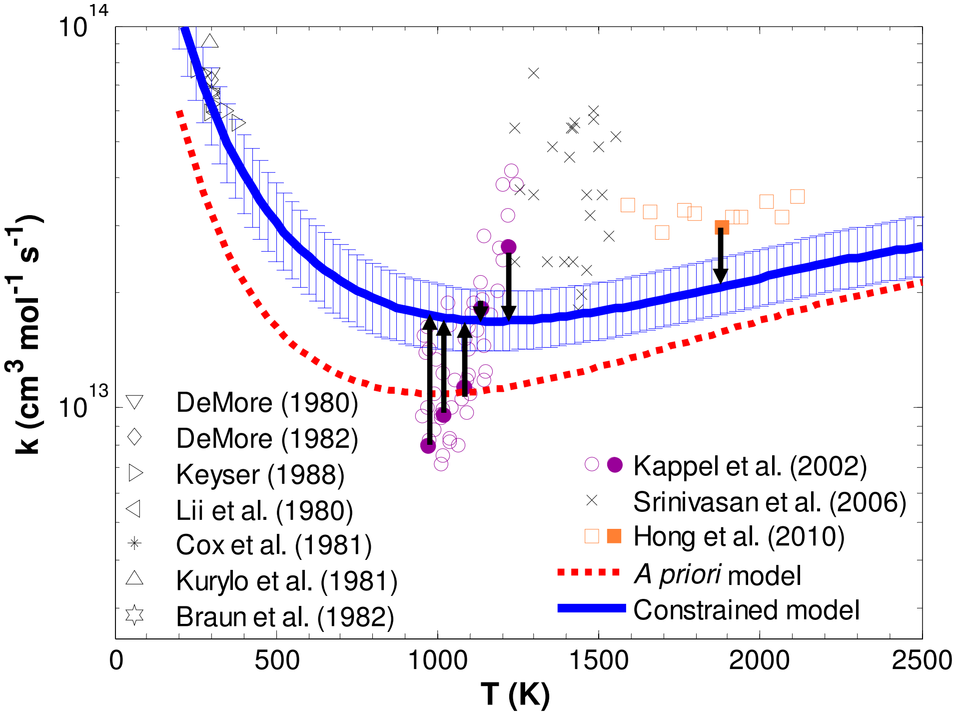

- *Simultaneous weighting* of diverse data types
  - Theory guides experimental interpretations
- Raw data and careful documentation extremely powerful

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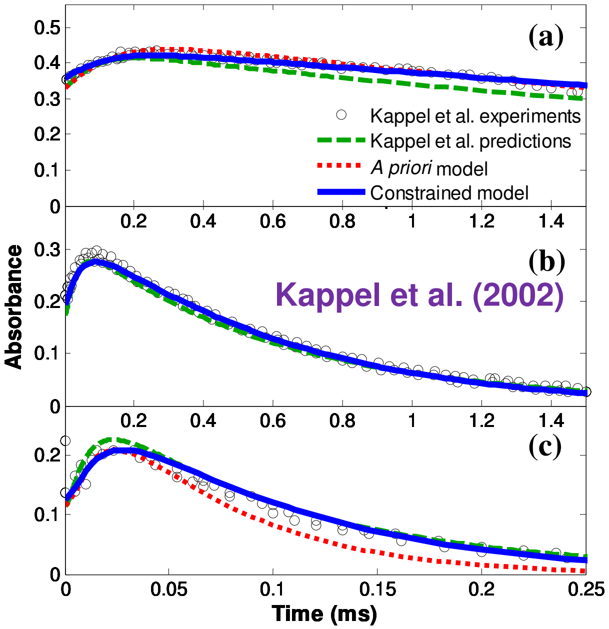

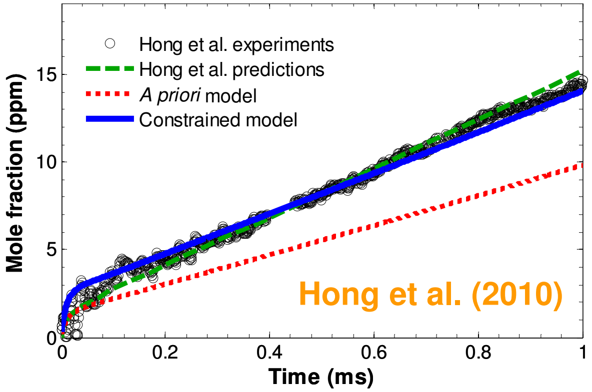

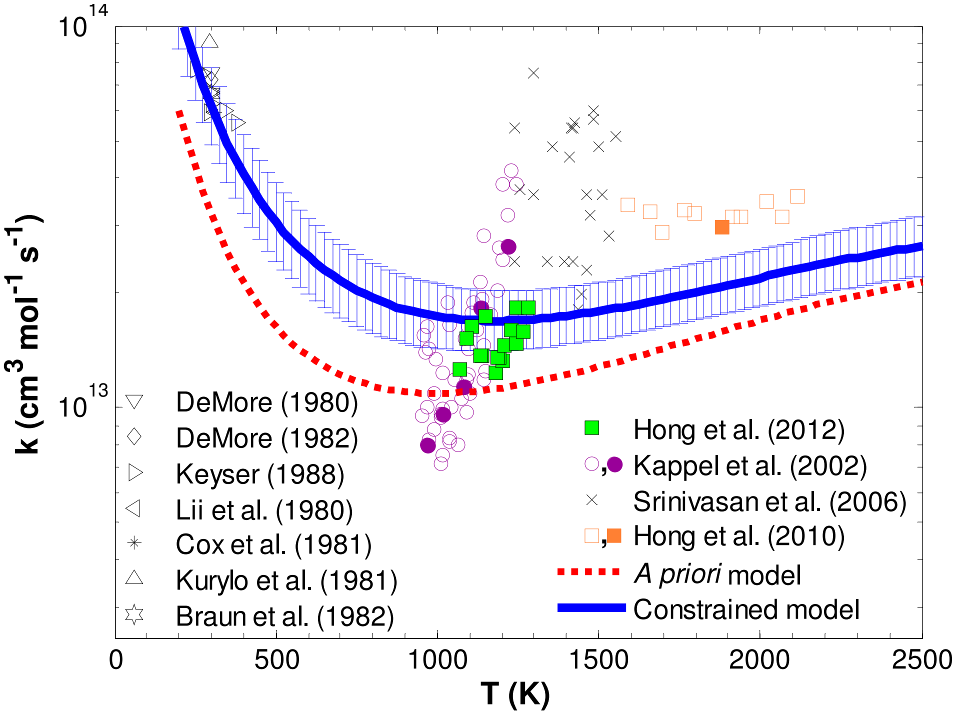

Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson

"On the rate constants of $OH + HO_2$ and $HO_2 + HO_2$: A comprehensive study of H_2O_2 thermal decomposition using multi-species laser absorption."

Combustion Symposium: 5D11

M.P. Burke, S.J. Klippenstein, L.B. Harding

"A quantitative explanation for the *apparent* anomalous temperature dependence of $OH + HO_2 = H_2O + O_2$ through multi-scale modeling."

Combustion Symposium: 4D09

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1. M.P. Burke, S.J. Klippenstein, L.B. Harding, *Proceedings of the Combustion Institute* (2012) in press.
2. Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson, *Proc Combust Inst* (2012) in press.

Conclusions

- High-pressure syngas flames
  - Emphasize HO_2 pathways + collision efficiencies of CO_2/H_2O
  - Inherently difficult to model
- Rigorous modeling solutions
  - Empirical adjustments based on global targets
  - Improved fundamental characterization
- Uncertainties remain in both 1) model parameters and 2) model assumptions
- Moving forward
  - Incorporation of theory to *fill in the gaps*
  - Raw data and careful documentation
  - Characterization of non-idealities/uncertainties in experiments and theory

Acknowledgements

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  - Director's Postdoctoral Fellowship from Argonne National Laboratory (MPB)
  - U. S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357 (SJK, LBH)
  - U. S. Department of Energy, University Turbine Systems Research Program under Contract No. DE-NT0000752 (FLD,YJ)
  - U.S. Department of Energy, Office of Basic Energy Sciences, Energy Frontier Research Center under Contract No. DE-SC0001198 (FLD,YJ)

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Thank you.

Questions?

End