Reduced and Validated Kinetic Mechanisms for Hydrogen-CO-Air Combustion in Gas Turbines

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Motivation

- General opinion that CO-H_2-O_2 kinetics are well understood and the underlying H_2 models are essentially the same within reasonable uncertainties…except at high pressures.
  - Recent examples:
    - *Sivaramakrishnan et al. (2007); Chaos and Dryer (2008): HO_2+OH*
    - *Mittal et al. (2006): HO_2+CO*
    - *Tse et al. (2000), Sun et al. (2007), Natarajan et al. (2009): flames*
- *Various model ignition delay predictions similar, and different than real observations in the mild ignition regime (Chaos and Dryer; 2008; Chaos et al., 2009).*
- Here we compare model performances at gas turbine conditions for burning rates.
  - Measure flame speeds/burning rates of H_2/O_2 mixtures over:
    - Lean and rich
    - Pressure: 1 to 25 atm
    - Flame temperature: 1500K to 1800K (typical lean conditions for NO_x control)
  - Compare measurements to recent models
- Results force exploration of kinetic pathways as pressure is increased.
- Identify likely sources of disagreement amongst models and with experiments.
- *Progress toward validated kinetic model revisions that improve prediction of high pressure flame behavior while maintaining other predictive abilities*
- *Develop approaches for improving computational efficiencies with detailed kinetics*

1. M. Chaos and F.L. Dryer, *Combust. Sci. Tech.* 180 (2008) pp1051-1094.
2. M. Chaos, M.P. Burke, Y. Ju, F.L. Dryer, Syngas chemical kinetics and reaction mechanisms, in: T.C. Lieuwen, V. Yang, R.A. Yetter (Eds.), *Synthesis Gas Combustion: Fundamentals and Applications*, Taylor & Francis, 2009, pp. 29–70.

Research Tasks

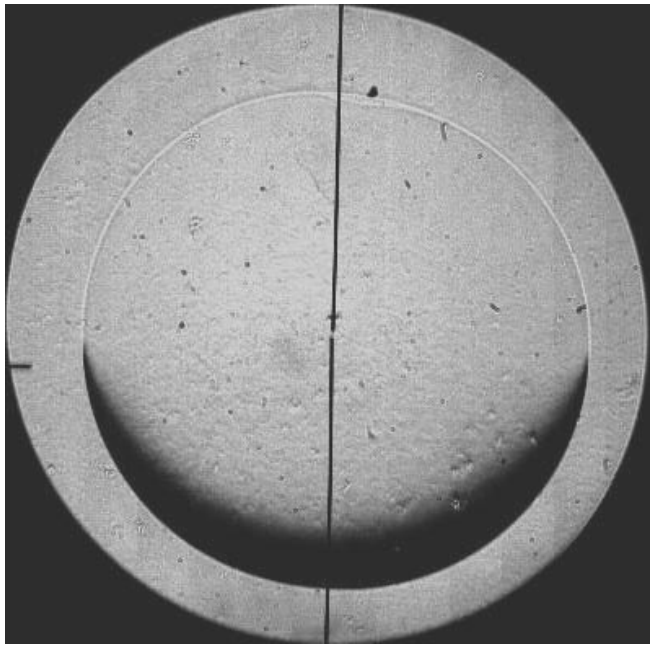
Methodology to measure flame speeds at high pressure

Flame speed measurements and mechanism validation

Dynamic Multi-Time Scale (MTS) kinetic computational method

1. Methodology to rigorously measure laminar flame speeds

Experimental Methods (I): Technique



(Taylor 1991, Faeth & co-workers 1992)

Stretch-corrected burning velocities from outwardly propagating flames at constant-pressure

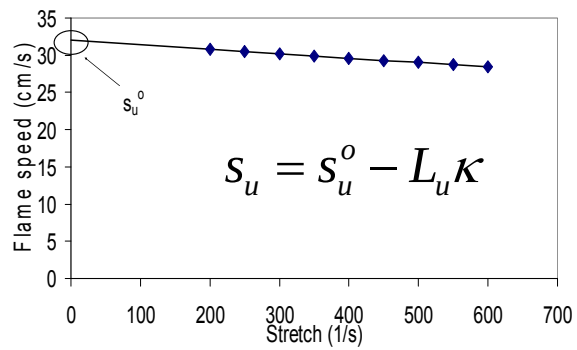
1. S.C. Taylor, *Phd. Thesis (Leeds University)*, 1991.
2. G.M. Faeth & co-workers 1992.

Constant-Pressure Method:

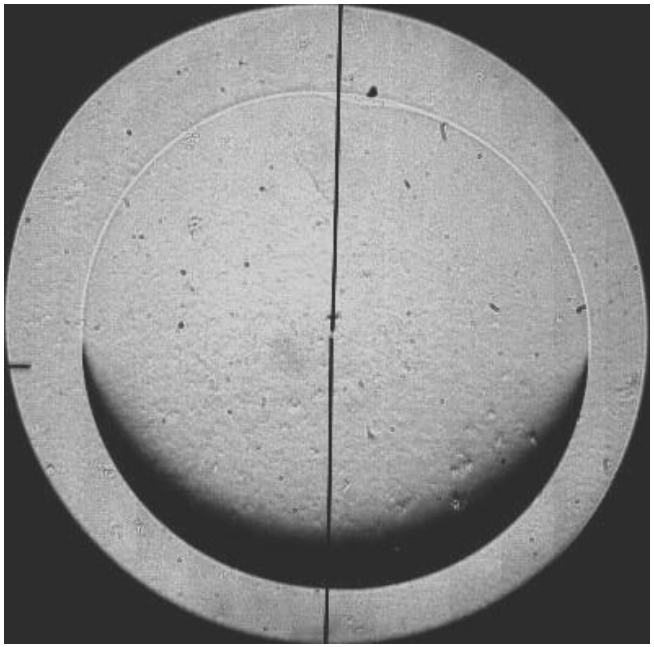
- Ignite at the center
- High-speed schlieren pictures of flame propagation
- Measure r_f vs. t
- *Usually* flame speed is calculated assuming no confinement:

$$s_u = \frac{\rho_b}{\rho_u} \cdot \left(\frac{dr_f}{dt} - \cancelto{0}{u_b} \right) \qquad \kappa = \frac{2}{r_f} \cdot \frac{dr_f}{dt}$$

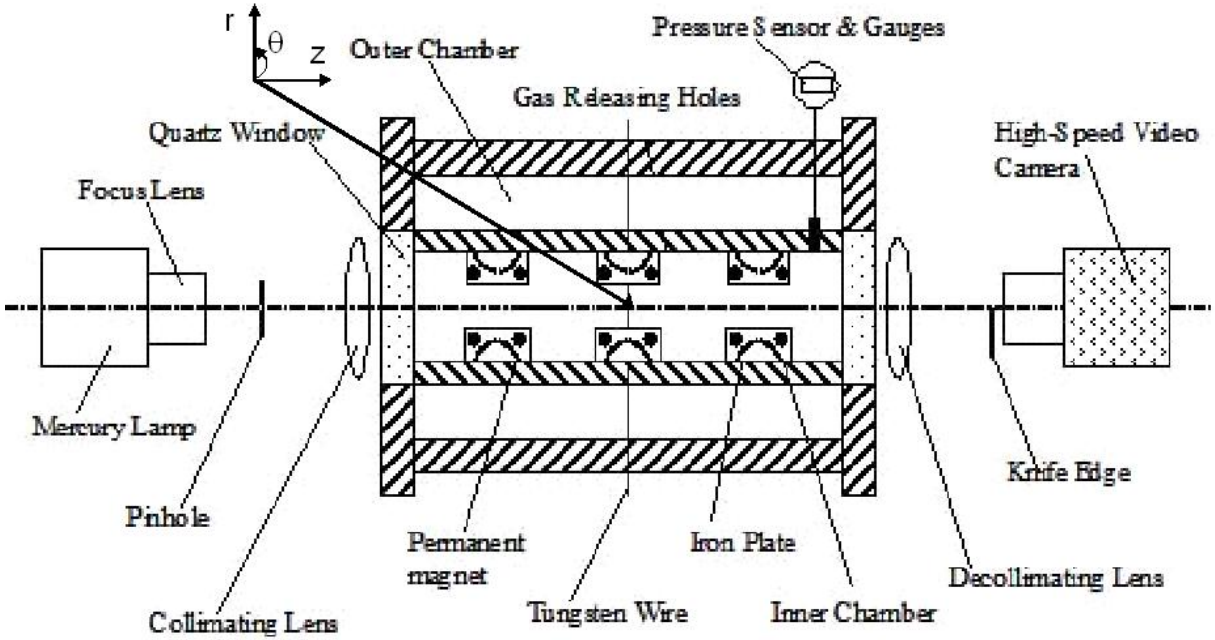
- Extrapolate to zero stretch rate



Experimental Methods (II): Apparatus



(Taylor 1991, Faeth & co-workers 1992)



(Tse et al. 2000, Qin & Ju 2005)

Stretch-corrected burning velocities from outwardly propagating flames at constant-pressure

- Present experiment *(Qin & Ju 2005)*:
  - Dual-chambered cylindrical bomb
  - Initial pressures up to 30 atm
  - Dimensions: 10 cm dia. by 15 cm length
- Law et al., others use similar geometries

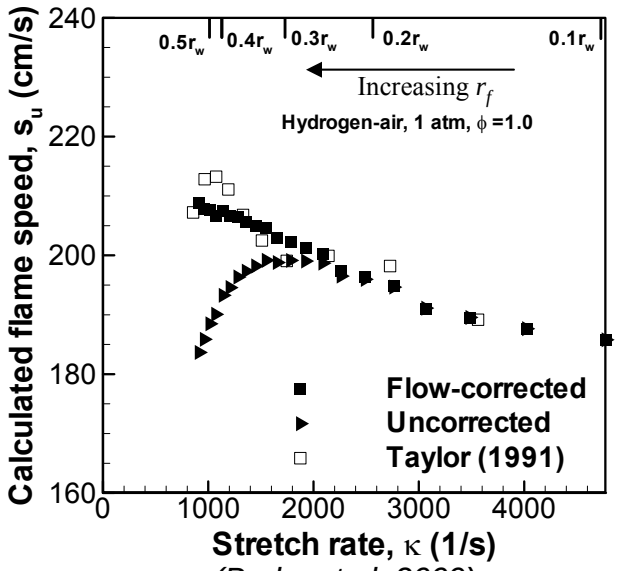
1. S.C. Taylor, *Phd. Thesis (Leeds University)*, 1991.
2. G.M. Faeth & co-workers 1992, and others.
3. S.D. Tse, D.L. Zhu, C.K. Law, *Proc. Combust. Inst.*, 2000.
4. X. Qin & Y. Ju, *Proc. Combust. Inst.*, 2005.

Experimental Methods (III): Improved Methodologies

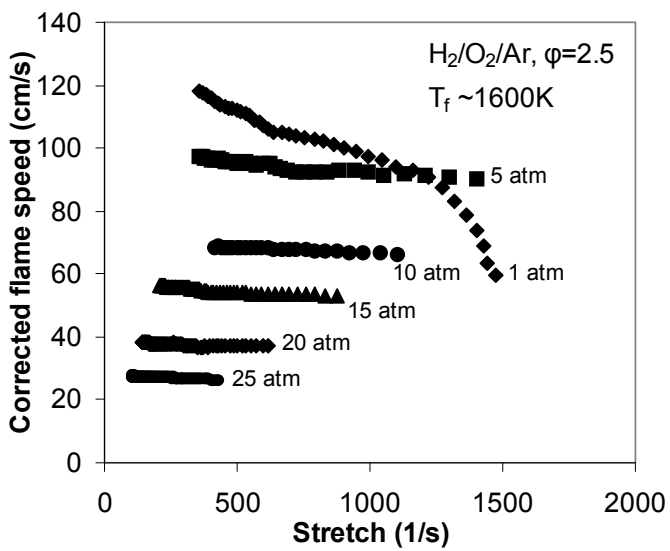
- Burned gas velocity not zero at large r_f even at constant pressure!
  - If possible, use $r_f < 0.3r_w$
  - If not, use flow correction:

Correction term

$$s_u = \frac{\rho_b}{\rho_u} \cdot \left(\frac{dr_f}{dt} - u_b \right) = \frac{\rho_b}{\rho_u} \cdot \frac{dr_f}{dt} \left(1 + \frac{\rho_u - \rho_b}{\rho_u} \varpi \right)^{-1}$$



(Burke et al. 2009)



(Chen et al. 2009)

- Unsteady/nonlinear effects in high Le & Ze flames up to *1.5 cm* ($0.3r_w$)
  - Restrict data range for analysis to quasi-steady flames where flame speed responds linearly to stretch

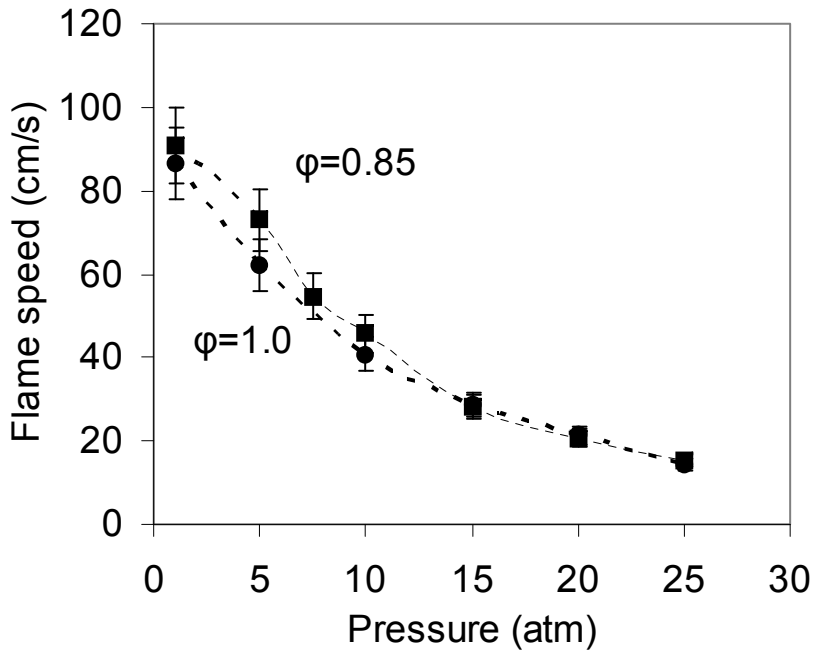
1. M.P. Burke, Z. Chen, Y. Ju, F.L. Dryer, *Combust. Flame*, 156 (2009) 771–779.
2. Z. Chen, M.P. Burke, Y. Ju, *Proc. Combust. Inst.* 32 (2009) 1253–1260.

2. A. Flame speed measurements & kinetic mechanism for H_2/O_2 and $CO/H_2/O_2$

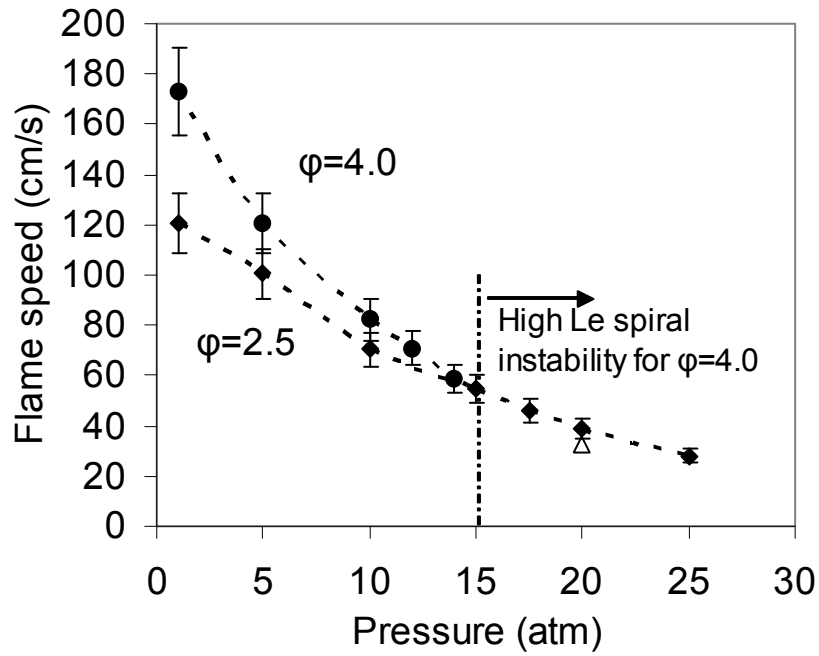
Experimental Data ($H_2/O_2/He/Ar$):

Flame Speed vs. Pressure

Lean $H_2/O_2/He$ of Flame Temp=1600K



Rich $H_2/O_2/Ar$ or N_2 of Flame Temp=1600K



- Flame speed decreases uniformly with pressure.
- Flame speed becomes less dependent on mixture composition and more dependent on flame temperature at high pressure.

1. M.P. Burke, Z. Chen, Y. Ju, F.L. Dryer, *Combust. Flame*, 156 (2009) 771–779.

Mass Burning Rates and Global Kinetics

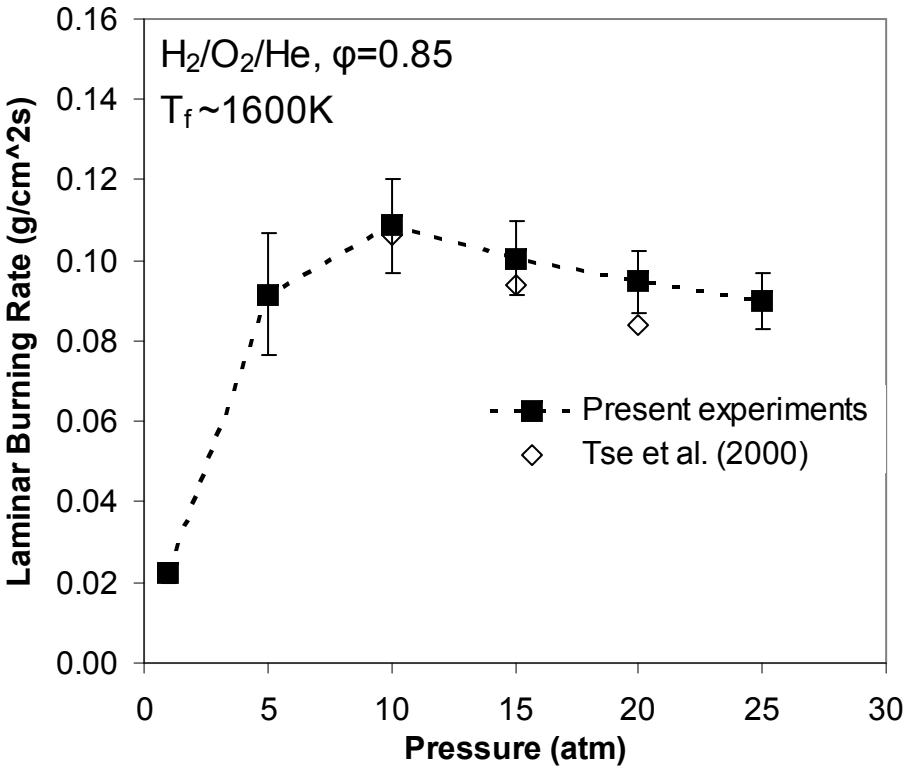
- Definitions
  - Mass burning rate: $\dot{m}^o = \rho_u s_u^o$
  - Global reaction rate: $\omega \sim p^n \exp(-E_a / RT_f)$
  - Global reaction order: $n = 2\left\{\frac{\partial ln(\dot{m}^o)}{\partial ln(p)}\right\}_{Tf}$
  - Global activation energy: $E_a = -2R\left\{\frac{\partial ln(\dot{m}^o)}{\partial ln(1/T_f)}\right\}_p$
- Pressure dependence of m^o due to kinetics

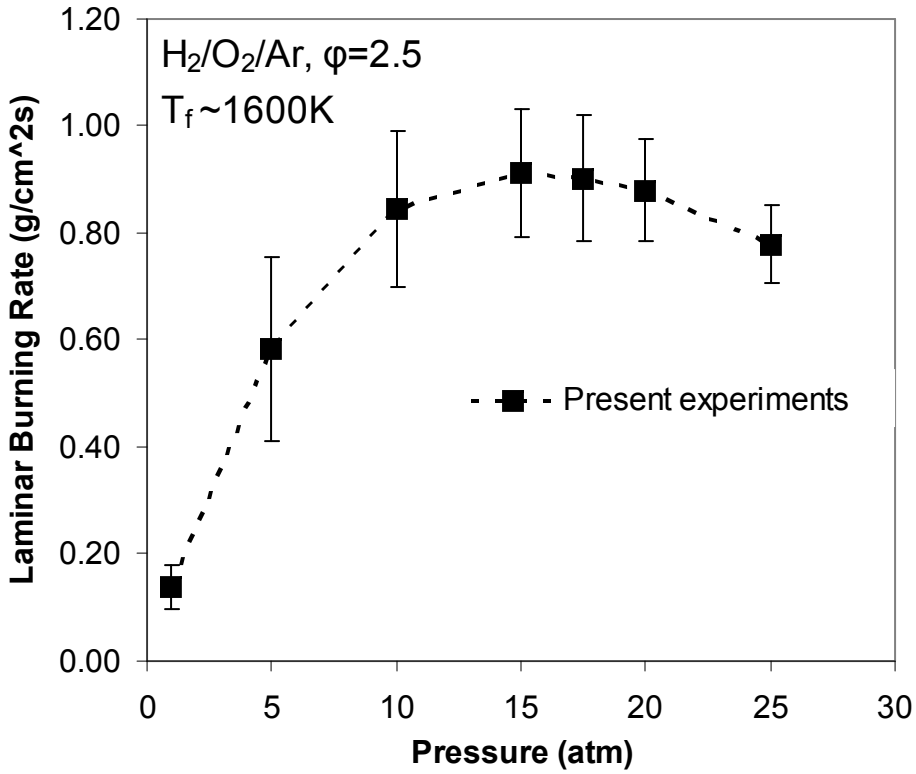
$$\dot{m}^o \sim \omega^{1/2} \sim p^{n/2} exp(-E_a / 2RT_f)$$

1. F.N. Egofopoulos, C.K. Law, Combust. Flame 80 (1990) 7–16.

Pressure Dependence of Mass Burning Rate

$$\dot{m}^o \sim \rho_u s_u^o \sim \omega^{1/2} \sim p^{n/2} exp(-E_a / 2RT_f)$$

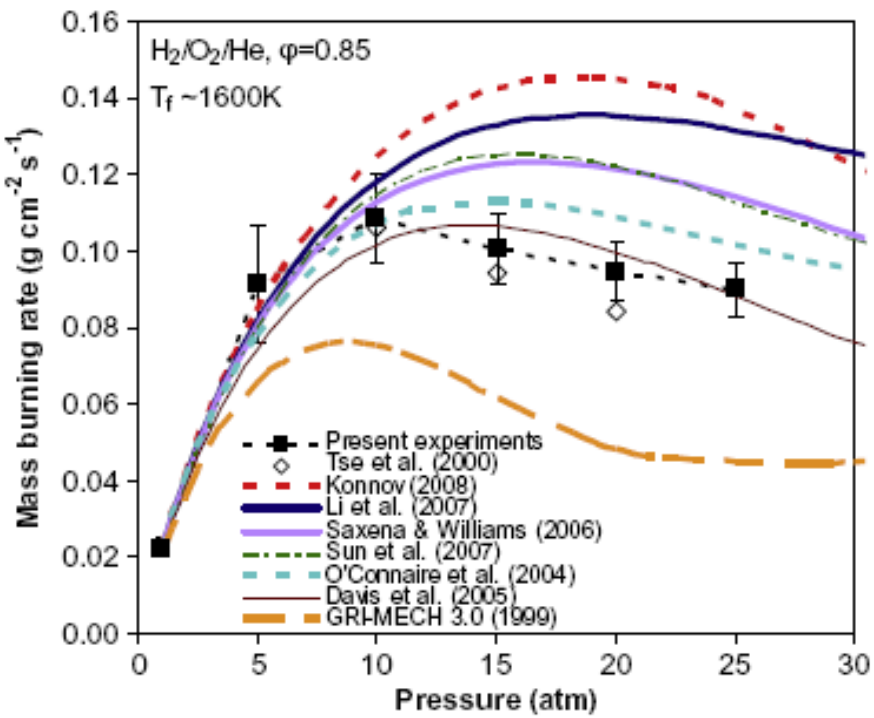


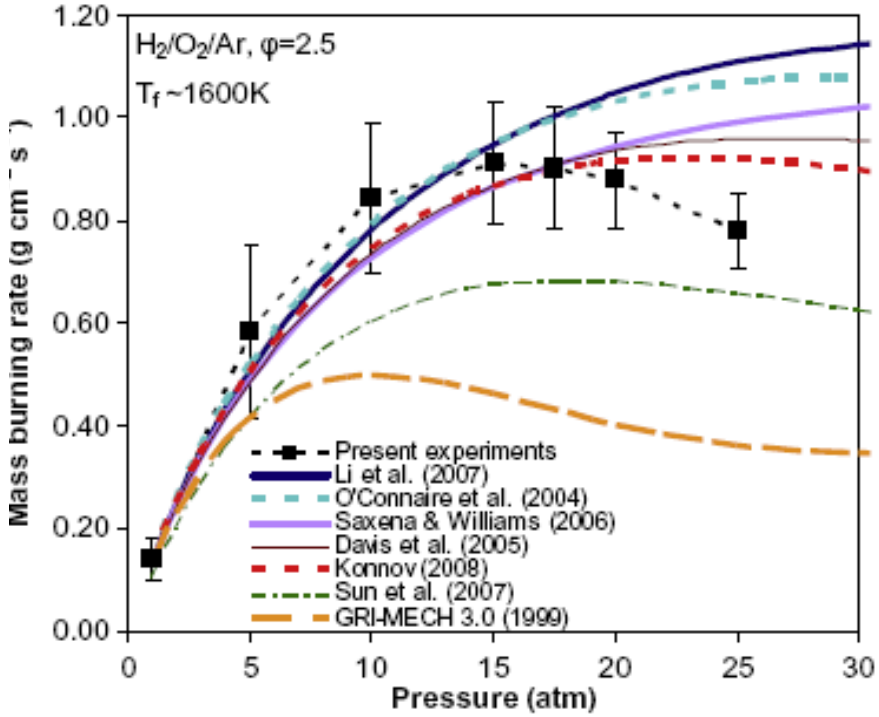


- Mass burning rate increases, then decreases with pressure
- Lean data consistent with earlier results of Tse et al. (2000).

1. S.D. Tse, D.L. Zhu, C.K. Law, Proc. Combust. Inst. 28 (2000) 1793–1800.

Comparison with Recent Kinetic Models

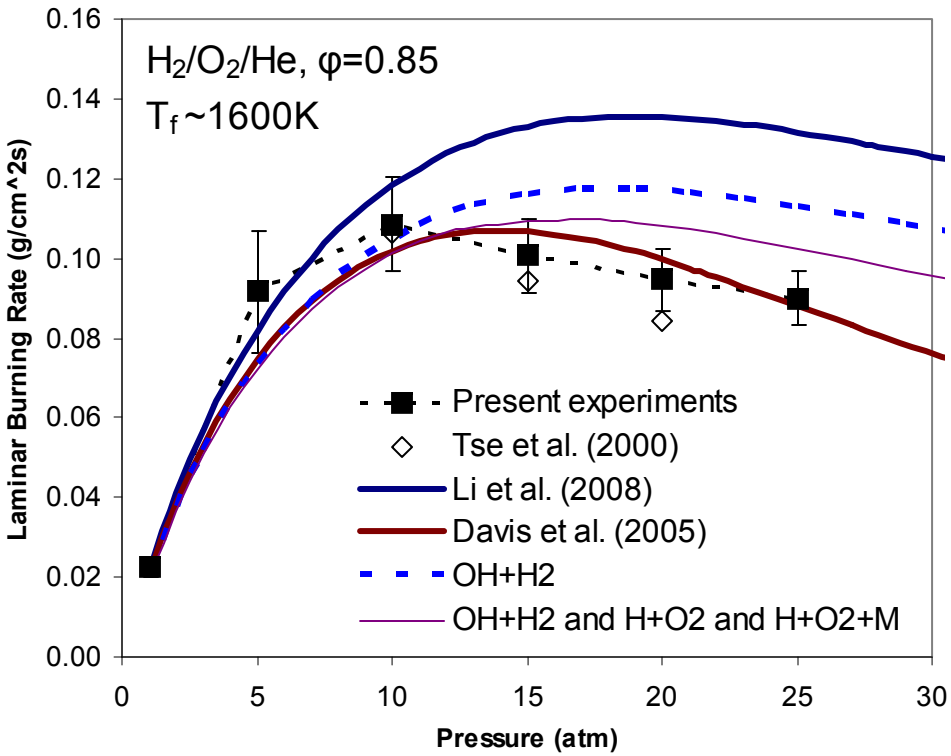




- Large variations among model predictions at higher pressures and all equivalence ratios
- None of the models capture pressure dependence across equivalence ratio

1. J. Li, A. Kazakov, Z. Zhao, M. Chaos, F.L. Dryer, J.J. Scire, *Int. J. Chem. Kinet.* 39(2007) 109–136.
2. S.G. Davis, A. Joshi, H. Wang, F.N. Egolfopoulos, *Proc. Combust. Inst.* 30 (2005) 1283–1292.
3. H.Y. Sun, S.I. Yang, G. Jomaas, C.K. Law, *Proc. Combust. Inst.* 31 (2007) 439–446.
4. A.A. Konnov, Combust. Flame 152 (2008) 507–528.
5. M. O'Connaire, H.J. Curran, J.M. Simmie, W.J. Pitz, C.K. Westbrook, I*nt. J. Chem. Kinet.* 36 (2004) 603–622.
6. P. Saxena, F.A. Williams, *Combust. Flame* 145 (2006) 316–323.
7. GRI-MECH 3.0. <http://www.me.berkeley.edu/gri_mech/>.

Why Does Davis Capture Pressure Dependence Better for φ=0.85?

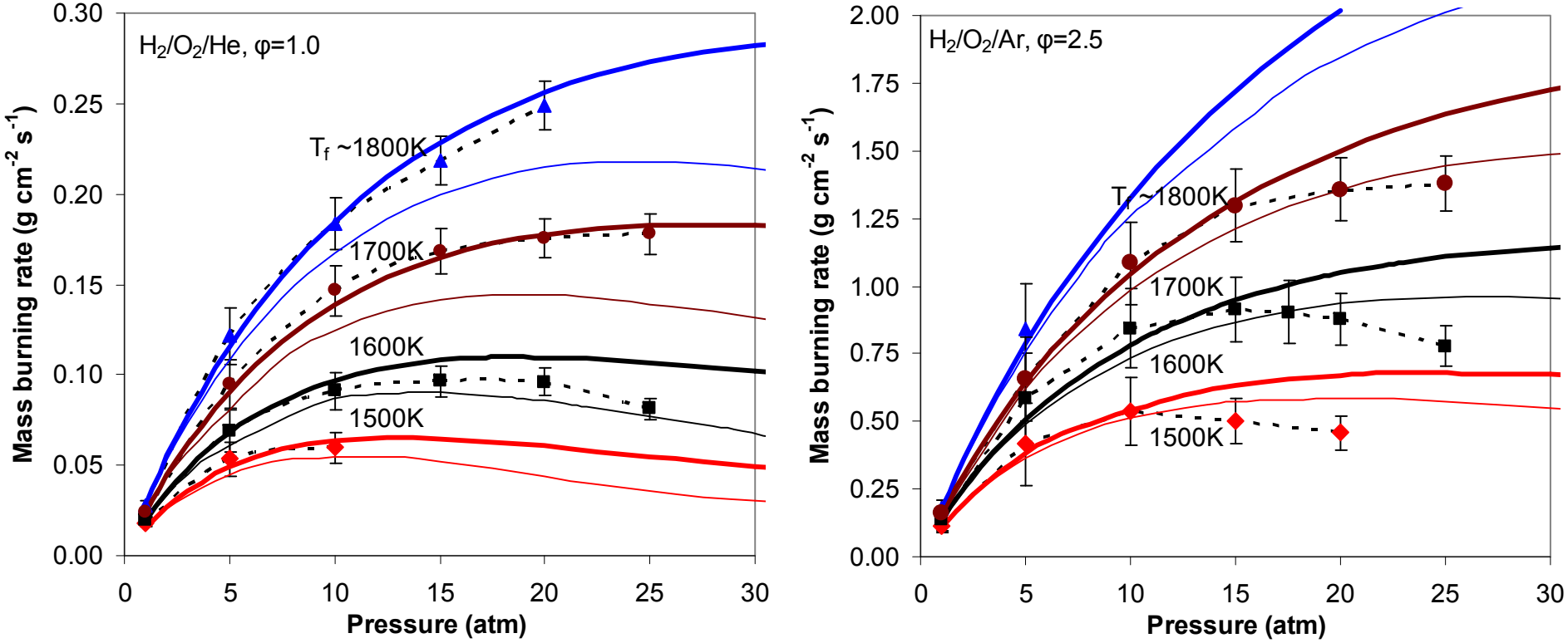


- Davis et al (2005) is a model that was "optimized against flame speed by varying rate parameters within their uncertainty limits.
- Some parameters were driven to essentially their uncertainty limits in the optimization.
- Shows 2 hybrid models that are the model of Li et al. (2007) with the indicated reactions substituted from Davis et al (2005).

- Most of the difference due to:
  - $OH+H_2=H_2O+H$
  - $H+O_2=OH+O$
  - $H+O_2+M=HO_2+M$
  - **These three reactions are still unconstrained!**
- Substitution of the $H+HO_2$ reactions from Davis et al. makes no difference

1. J. Li, A. Kazakov, Z. Zhao, M. Chaos, F.L. Dryer, J.J. Scire, *Int. J. Chem. Kinet.* 39 (2007) 109–136.
2. S.G. Davis, A. Joshi, H. Wang, F.N. Egolfopoulos, *Proc. Combust. Inst.* 30 (2005) 1283–1292.
3. S.D. Tse, D.L. Zhu, C.K. Law, *Proc. Combust. Inst.* 28 (2000) 1793–1800.

Effect of Flame Temperature

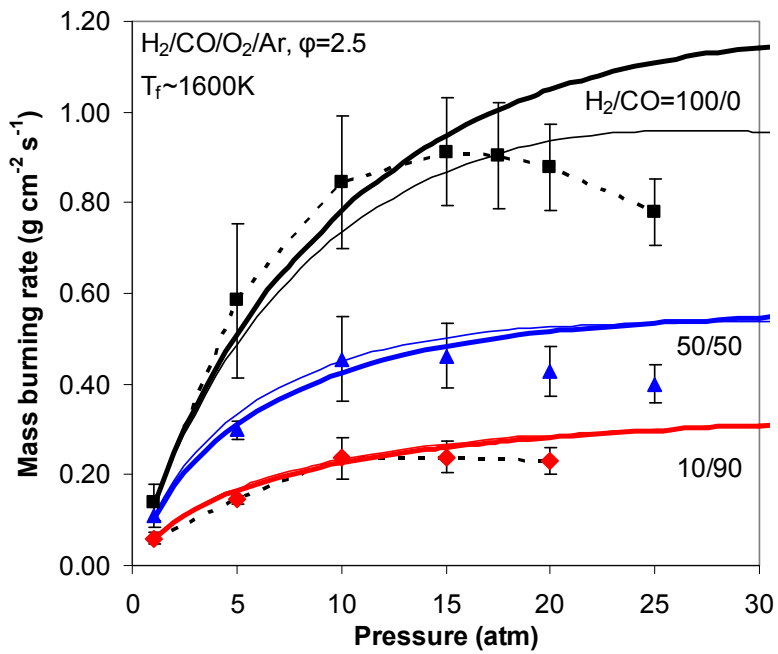


Bold lines: J. Li, A. Kazakov, Z. Zhao, M. Chaos, F.L. Dryer, J.J. Scire, *Int. J. Chem. Kinet.* 39 (2007) 109–136.

Thin lines: S.G. Davis, A. Joshi, H. Wang, F.N. Egolfopoulos, *Proc. Combust. Inst.* 30 (2005) 1283–1292.

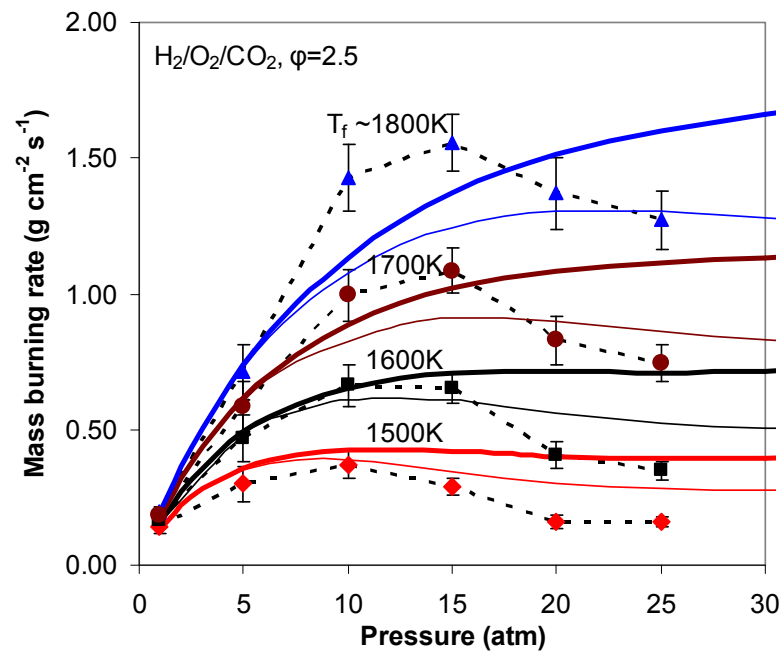
- Negative pressure dependence stronger at lower flame temperatures
  - Occurs at lower pressures
- Model performance worse at lower flame temperatures

Effect of CO Addition to Fuel



- Same trends as pure H_2 even up to 50% CO in fuel

Effect of CO_2 Dilution



- In comparison to Ar, CO_2 has high third body efficiency (~4)
  - Strengthens pressure dependence
- *Water has a much higher third body efficiency*
  - *Expect water dilution will cause further strengthening*

Bold lines: J. Li, A. Kazakov, Z. Zhao, M. Chaos, F.L. Dryer, J.J. Scire, *Int. J. Chem. Kinet.* 39 (2007) 109–136.

Thin lines: S.G. Davis, A. Joshi, H. Wang, F.N. Egolfopoulos, *Proc. Combust. Inst.* 30 (2005) 1283–1292.

Questions Prompted by Results

- What causes the negative pressure dependence?
- How can such extensively validated models be so unconstrained?
- What improvements can be made to reconcile disagreement of models with experimental data?
  - Davis does reasonably well for lean conditions, but can a more scientifically-based solution be found?
    - What happens to *older* optimizations when new parameters estimates and uncertainties emerge?
    - *A-Factor optimization doesn't consider that perhaps uncertainties in temperature dependence of specific reactions may be important.*
  - Do more refined literature estimates of elementary reaction rates improve predictions of the base model?
- Are there new reactions that become important for high pressure flames that have been overlooked in all of the prior published models?

2. B. Controlling kinetic pathways in high-pressure syngas flames

Effect of Pressure on Chemical Branching

- 3 body reactions favored

$$H + O_2 \rightarrow OH + O \quad (R1)$$

$$H + O_2 \xrightarrow{+M} HO_2 \quad (R2)$$

favored at lower pressures and higher temperatures

favored at higher pressures and lower temperatures

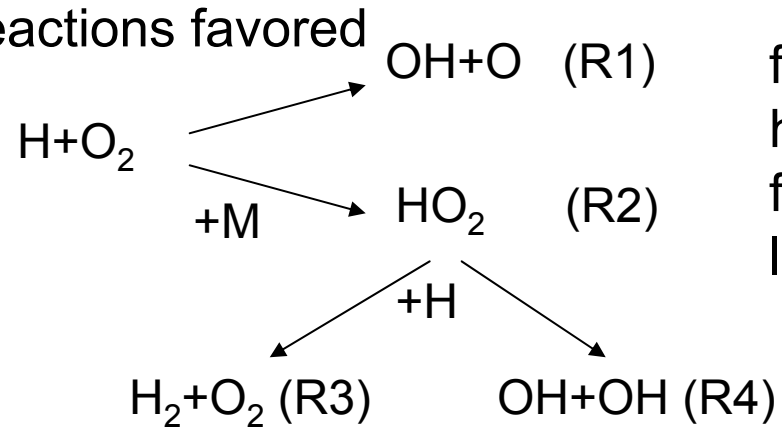
- (R2) is essentially "terminating" at low temperatures because the reactions involving HO_2 that could regenerate radicals are very slow and dominated by termination of HO_2.
  - Responsible for second explosion limit in homogenous kinetics for hydrogen oxidation

$$\frac{2k_1}{k_2[M]} < 1 \longrightarrow \text{Not explosive}$$

$$\frac{2k_1}{k_2[M]} > 1 \longrightarrow \text{Explosive}$$

Effect of Pressure and High Temperatures on Kinetics (II)

- 3 body reactions favored



favored at lower pressures and higher temperatures
favored at higher pressures and lower temperatures

- HO_2 paths are active at high P's and T's
  - R1/R2 competition still a major factor in pressure dependence of critical branching
  - Other HO_2 reactions modify termination and result in changing the branching required for the critical condition ("extended second explosion limit")

$$\frac{k_3+k_4}{2k_3}\frac{2k_1}{k_2[M]}<1 \longrightarrow \text{Chain-carrying (slow)}$$

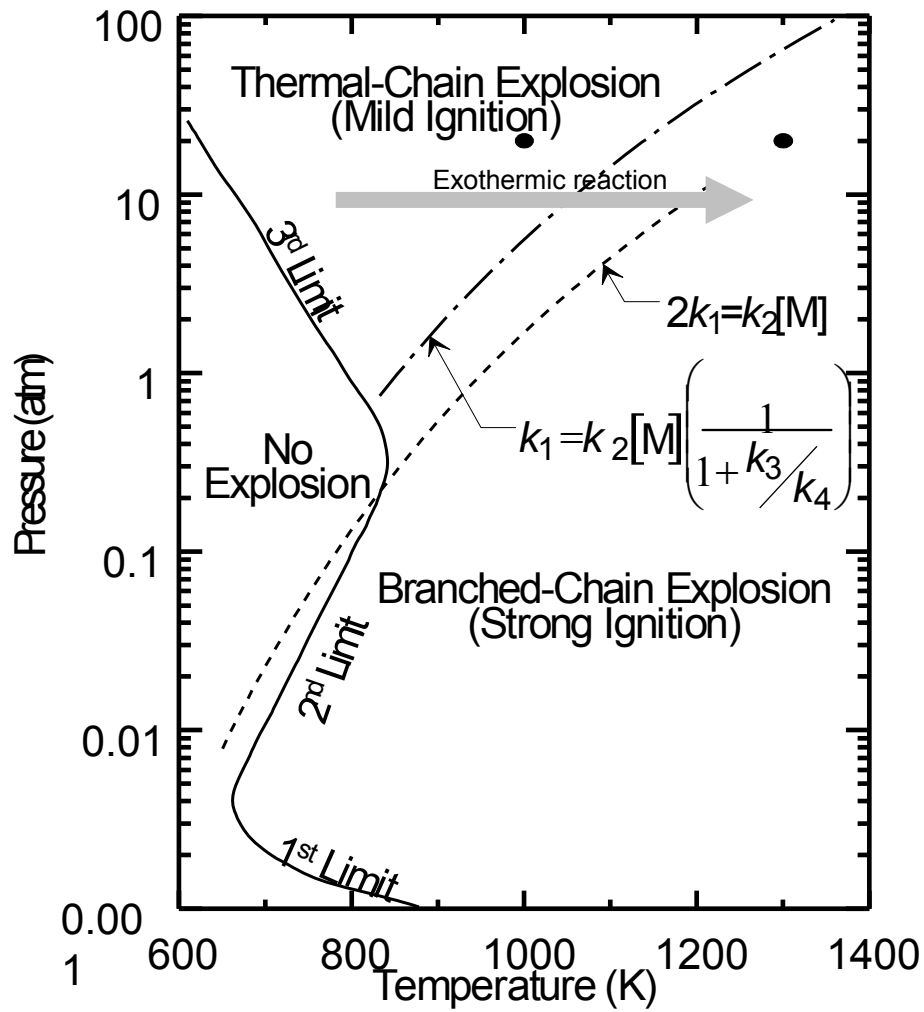
$$\frac{k_3+k_4}{2k_3}\frac{2k_1}{k_2[M]}>1 \longrightarrow \text{Chain-branching (fast)}$$

  - Observed in flow reactor and counter-flow ignition studies

1. M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, Int. J. Chem. Kinet. 31 (1999) 113–125.
2. X.L. Zheng, C.K. Law, Combust. Flame 136 (2004) 168–179.

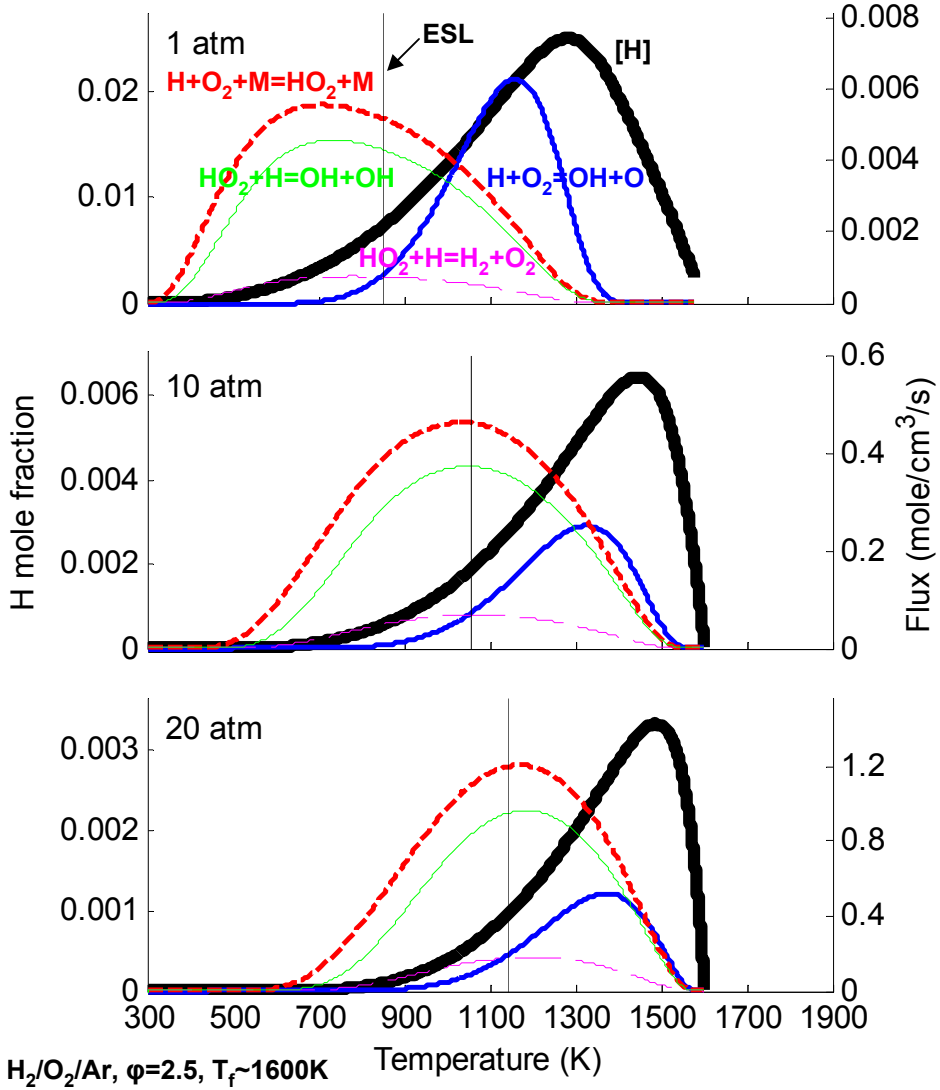
Explosion Limits

- For the same pressure, the extended second limit results reduced "termination" from HO_2 reactions and results in critical branching occurring at lower temperature.
- The reduction in termination is dependent on the rate constants of reactions that have significant uncertainties (k_3, k_4).
- Other species added to hydrogen oxidation can affect the rates of branching and termination and shift the pressure and temperature at which chemical branching becomes dominant in the oxidation.
- Instability analysis of this system shows highly sensitive region along the extended second limit boundary. (Yetter et, al., 1991)



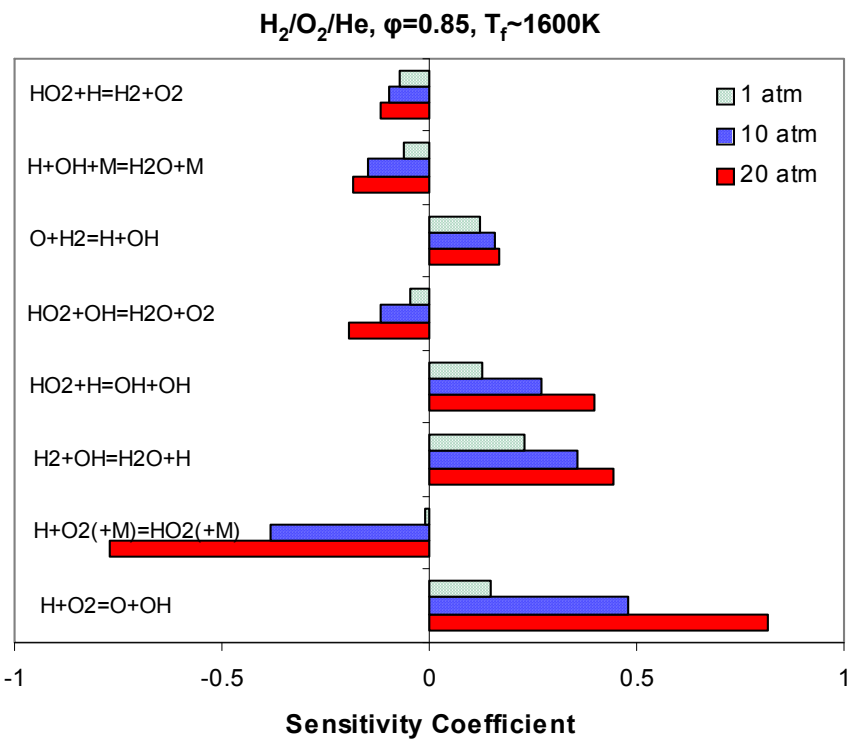
R.A. Yetter, H. Rabitz, and R.M. Hedges, Int. J. Chem. Kin. 23 (1991) 251-278.

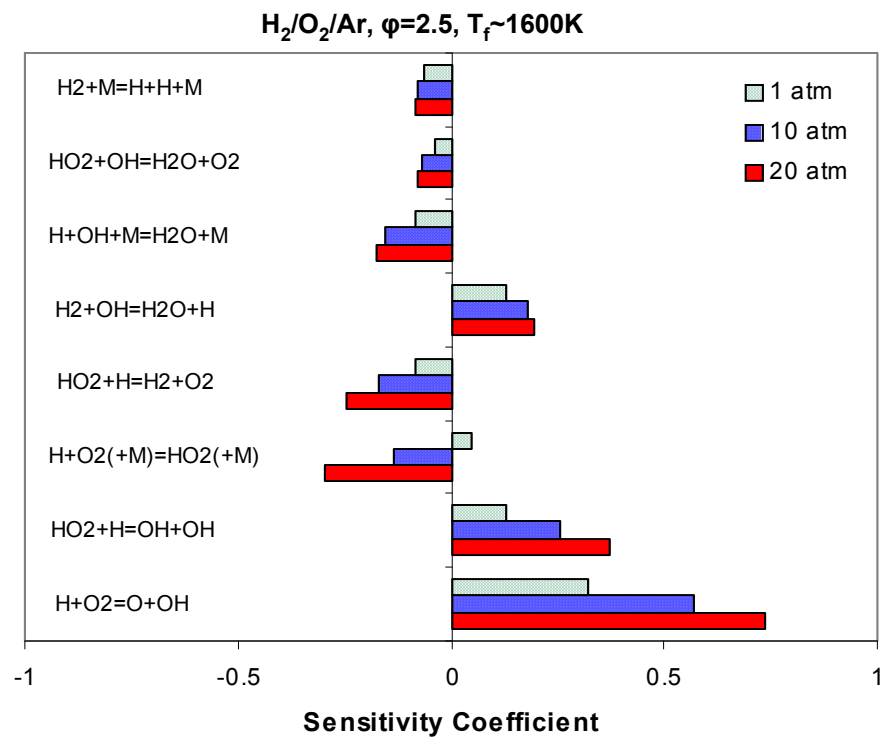
Effect of Pressure on H flux



- Extended Second Limit (ESL) is pushed to higher temperatures at higher pressures
  - Raises overall E_a
    - All radical and flux profiles shifted to higher temperatures
  - Increased flux through $H+O_2+M$ relative to $H+O_2$
  - Flux through $H+HO_2$
    - Increased significantly
    - Peaks at ~700K at 1 atm and ~1200K at 20 atm
- Similar behavior for fuel lean conditions

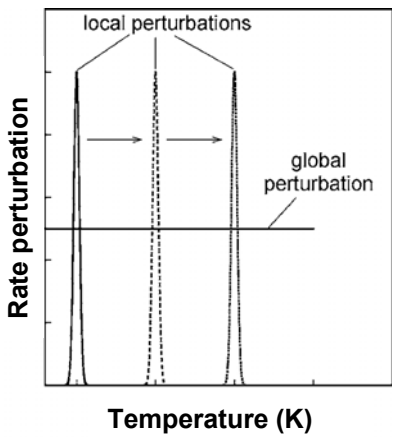
A-factor Sensitivity of Mass Burning Rate to Elementary Rates



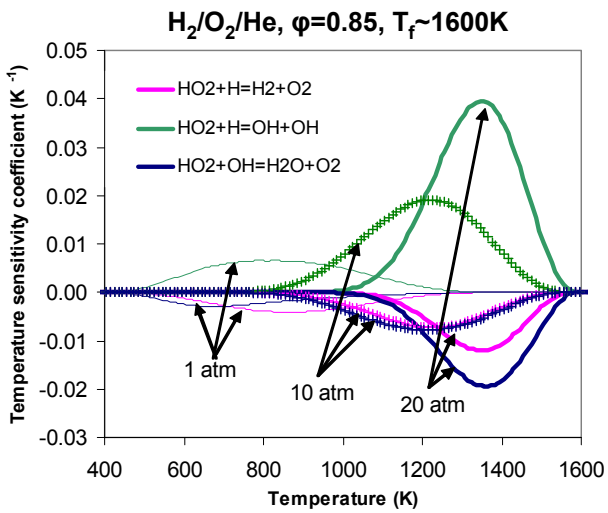


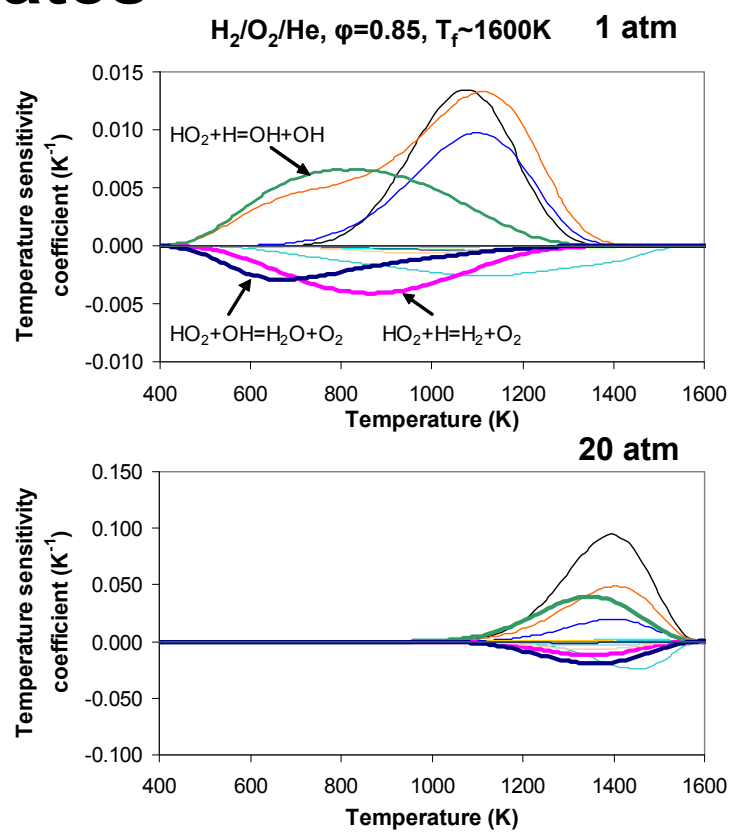
- Sensitivities of important reactions increase considerably with increasing pressure
- Pressure dependence governed by extended second limit reactions and H+OH+M = H_2O+M (in addition to OH+HO_2 and OH+H_2 for lean conditions)
- Rank ordering of the sensitivities is a function of equivalence ratio

Temperature Window Sensitivity to Elementary Rates



(Zhao et al. 2005)





- As pressure increases:
  - The most sensitive temperature for each reaction shifts toward higher values for all reactions *(Model optimization must include rate parameter temperature dependences)*
  - Location shifts the most for HO_2+H and HO_2+/OH reactions (700K to 1200K)
- Shapes of sensitivity curves change significantly with both pressure and equivalence ratio

1. Z. Zhao, J. Li, A. Kazakov, F.L. Dryer, Int. J. Chem. Kinet. 37 (2005) 282–295.

2. C. Improved rates for elementary reactions and updated H_2 model

Noted Important Reactions

(No particular order)

$H+O_2=OH+O$

$H+O_2(+M)=HO_2(+M)$

$OH+H_2=H_2O+H$

$O+H_2=OH+H$

$H+HO_2=OH+OH$

$H+HO_2=H_2+O_2$

$OH+HO_2=H_2O+O_2$

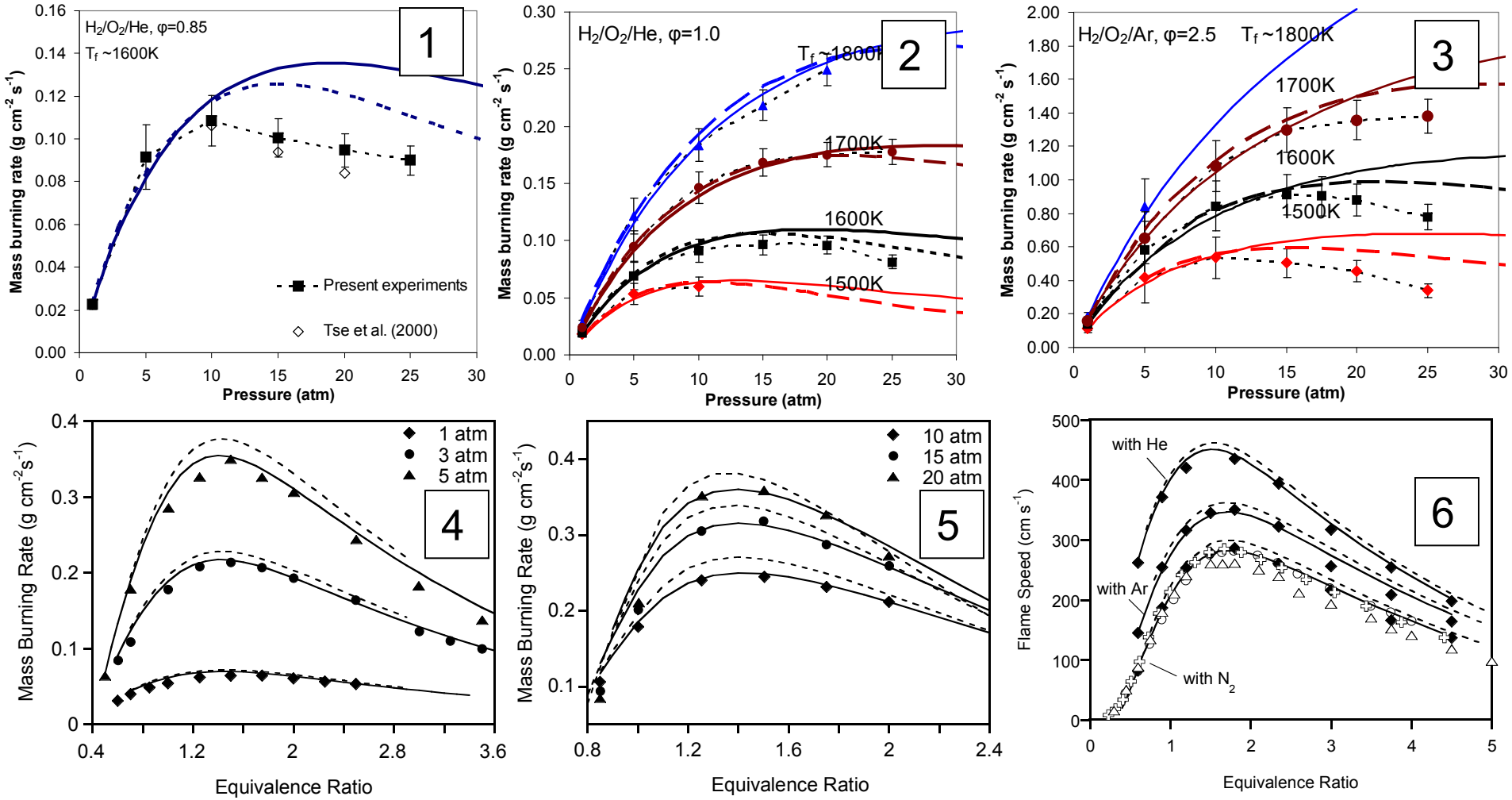
$H+OH+M=H_2O+M$

$O+OH+M=HO_2+M$

- Thermochemistry for species in this reaction system is well determined to small uncertainties and was not considered as a source of difficulties.
- Transport parameters are unlikely source for large uncertainties found in the burning rates.
- Numerous model configurations were investigated considering all of these reactions
- Improving predictive ability of the model cannot be achieved by modifications in one or two rate parameters, but requires consideration of multiple reactions and rate parameter selections

- *The Li et al. 2007 hydrogen/CO submodel parameters have been updated and will be published shortly (Contact the authors for further information).*
- *More recent rate parameters have been reviewed and the burning rate data along with earlier validation targets have been considered in the revisions.*
- *Comparisons of the updated model against these targets appear on the following slides.*

Flame Targets from Li et al. (2004) and Burke et al. (2009)

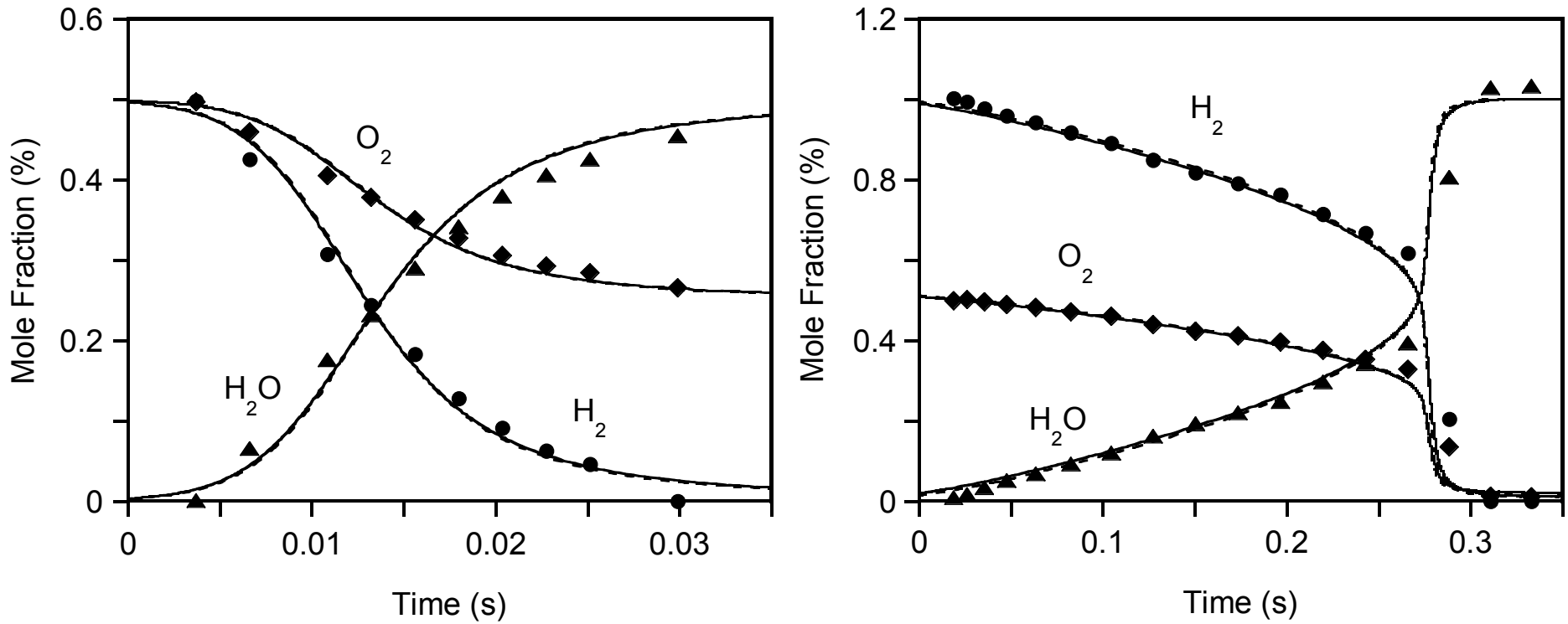


Solid lines: Li et al. 2007, Dotted lines: Updated H_2 model, experimental data for Figs. 1-3 from Burke et al. (2009), for Figs. 4-5 from Tse et al. (2000) used for validation in Li et al (2004).

J. Li, Z. Zhao, A. Kazakov, F.L. Dryer, Int J Chem Kinet 36 (2004) 566–575.

Targets from Mueller et al. (2000)

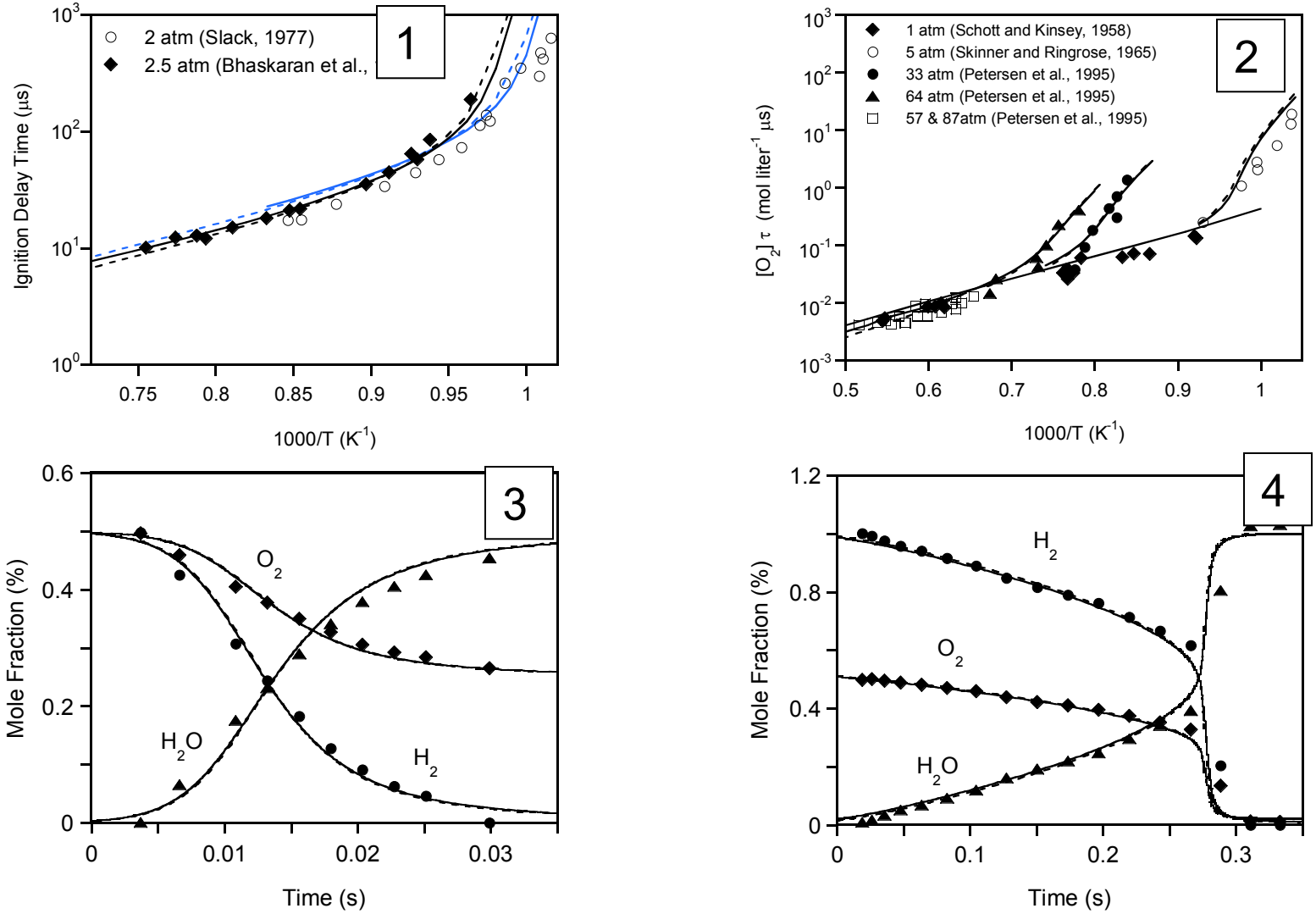
- Predictions using revised model are nearly indistinguishable from Li et al. 2007



Solid lines: Li et al. 2007, Dotted lines: Updated H_2 model

M. A. Mueller, R. A. Yetter, F. L. Dryer, Int J Chem Kinet 32 (2000) 317–339.

Ignition Targets as Utilized in Li et al. (2004)

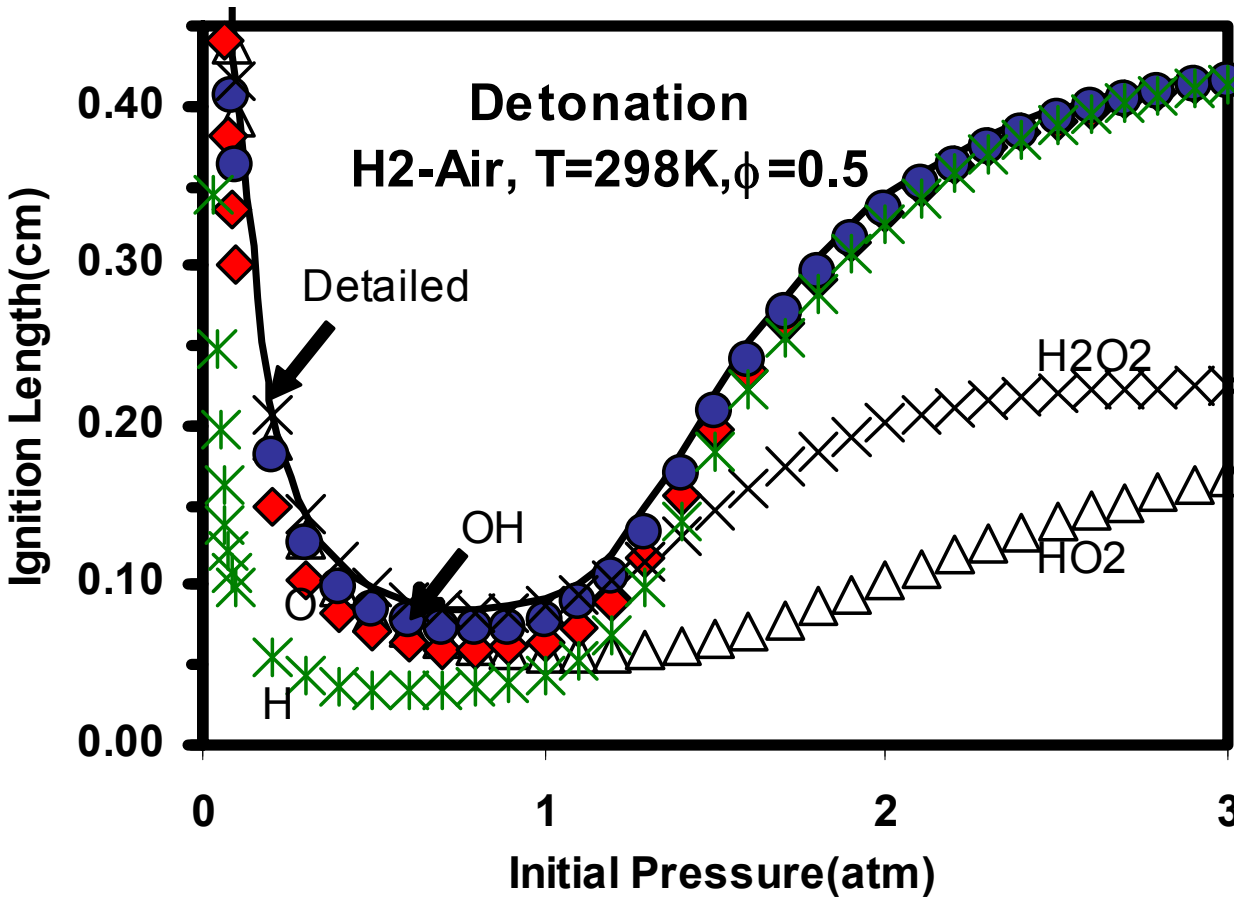


Solid lines: Li et al. 2007, Dotted lines: Updated H_2 model, experimental data for Figs. 3-4 from Mueller et al. (2000).

J. Li, Z. Zhao, A. Kazakov, F. L. Dryer, *Int. J. Chem. Kinet.* 36 (2004) 566–575.

3. Development of method for improving computational efficiency with detailed kinetic models.

Consideration of the Hydrogen Model Reaction Dynamics vs. QSS Assumptions



- **No species can be reduced! How to reduce chemistry size?**
- **Time scales are very different!**

The Problem

- Combustion problems are multi-scale in both time and length scales
  - Results in great difficulty in achieving computational efficiency with accuracy.
- Much of the problem comes from complexity of sub-models, especially combustion kinetics.
  - Typical real fuels (or fuels with NO_x and contaminant kinetics included) are composed of 50 to 1000's of species (n) and 100's to 10^4 reactions (r).
    - Hydrocarbon oxidations are especially large systems if one includes two stage ignition predictions.
    - H_2-CO-O_2 system cannot be reduced further; adding NO_x and contaminant chemistry will increase the number of species significantly.
  - Results in large data storage and computing power requirements, as well as data transfer complexities.
- Stiff equation solvers have addressed the multi-time scale issues of chemical kinetics, but are not very efficient
  - CPU time scales as n^2.
  - Explicit solver algorithms (e.g. Euler methods) require following even the smallest time and length scales to couple behavior of variables of interest. (Really severe problem for direct numerical simulations.)

General Methodology

- Typical on-grid operator splitting approach is to solve non reactive properties first, and then perform a point implicit fractional step procedure to solve for chemistry (stiff ODE method).
  - Implicit Euler (backward difference) methods addresses this problem with ODE differential equation solvers in stiff systems (stiff equation solvers) but are an expensive CPU time solution.
  - Explicit Euler methods are fast, but require smaller time scales to maintain accuracy.
    - Typical Time scale ranges – (reaction systems are intrinsically dynamic…)
      - Reaction initiation: 10^{-4} to 10^{-10} sec
      - Thermal runaway after ignition: 10^{-7} to 10^{-13} sec
    - An Euler explicit method would typically require time stepping at less than the smallest time scale to be accurate
- The Multi Time Scale (MTS) method permits use of Explicit Euler approach with accuracy maintained.
  - MTS replaces the second step above using an Euler Explicit, but multi time scale solution approach.
- MTS – Specify base time scale, T_{base} (related to the physical scale).
  - Define sub timescales to construct models for T_{base} observations.
  - Break up into sub time scales.
  - Perform Euler explicit solution at each sub time scale only for a few time steps to approach chemical dynamic state relative to it characteristic time of response, and then use the information to support integration of the next set of grouped quantities at the next larger time scale.

A Dynamic Multi-Scale (DMS) Kinetic Reduction Model

Time scales in reactive flow

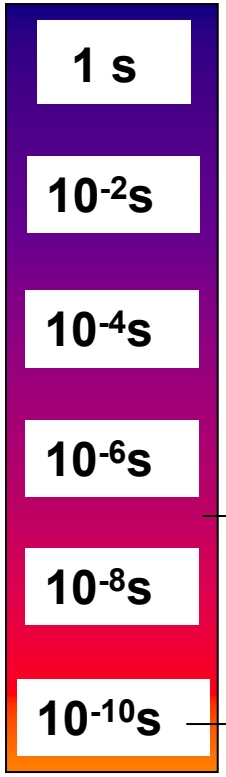
Chemical time

NO formation

Product formation H_2O

Radical formation H

Radical formation H_2O_2
quasi-steady state?



Physical time

Flow time

Transport time
Molecular
Turbulent

Physical interest

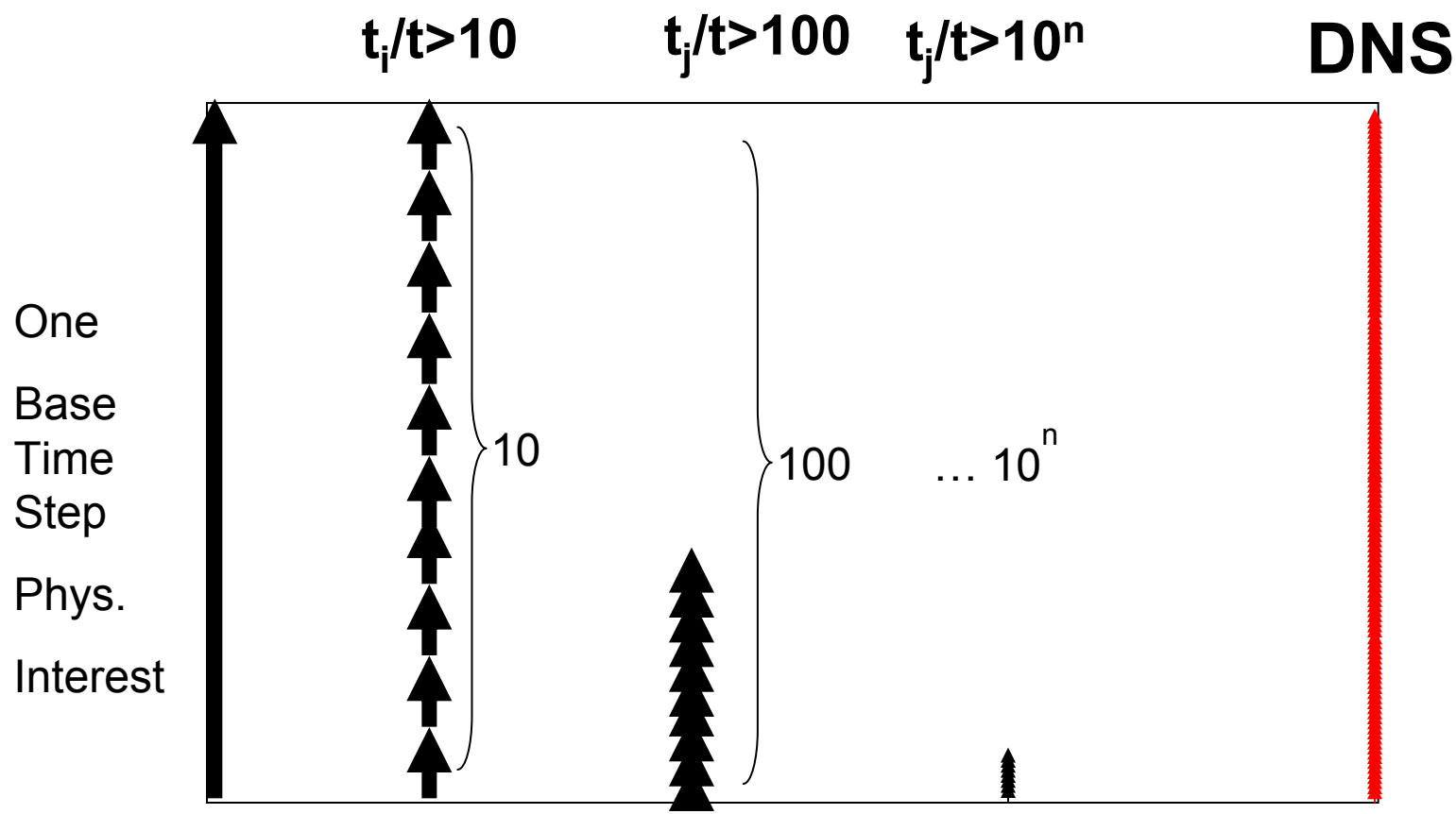
Radiation transfer
quasi-steady state

?

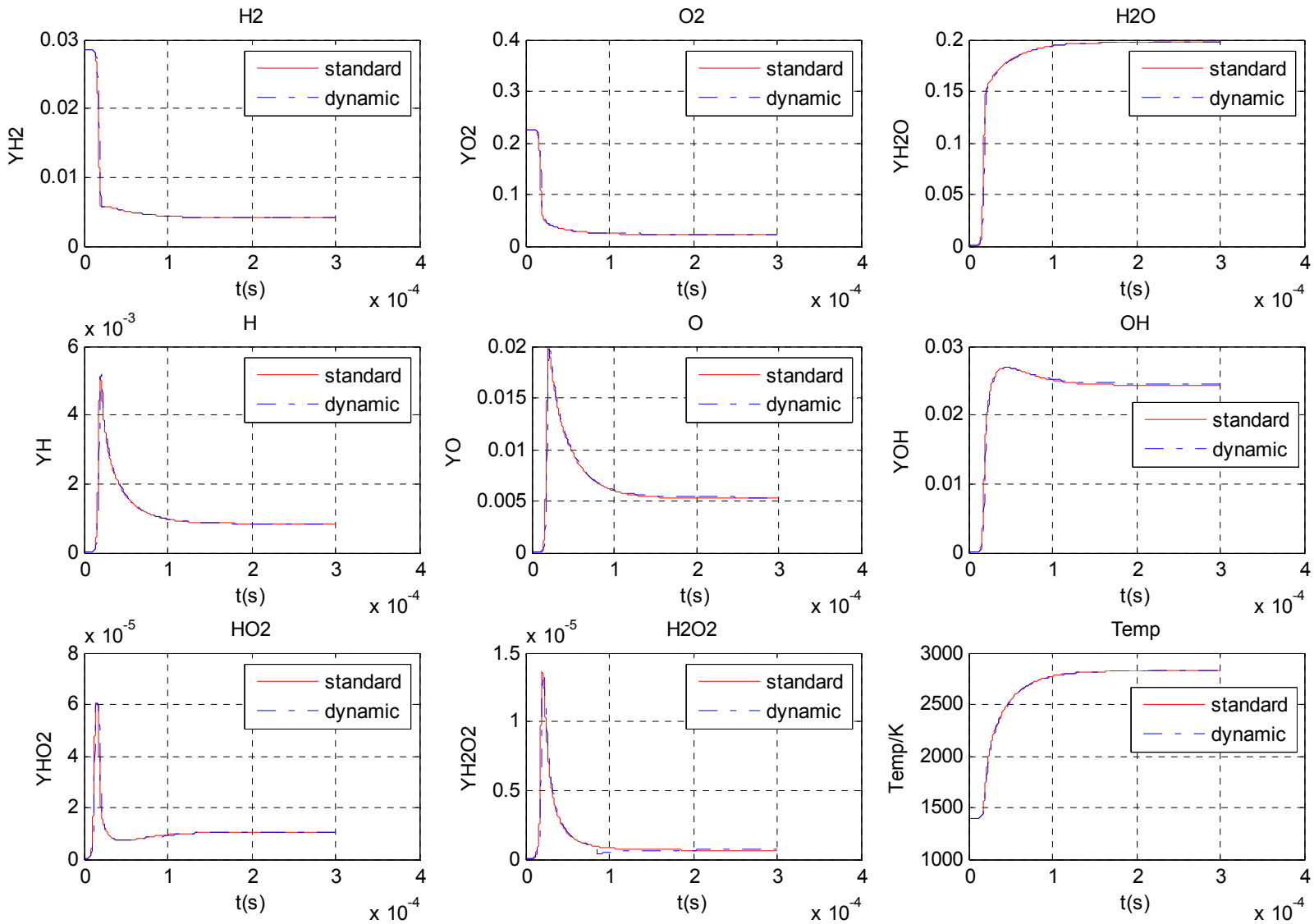
DNS Time-step

Algorithm of Dynamic Multi-Scale (DMS) Modeling

Every species decays at its own time scale: $Y_i = Y_{i0} e^{-\frac{t}{\tau_i}}$

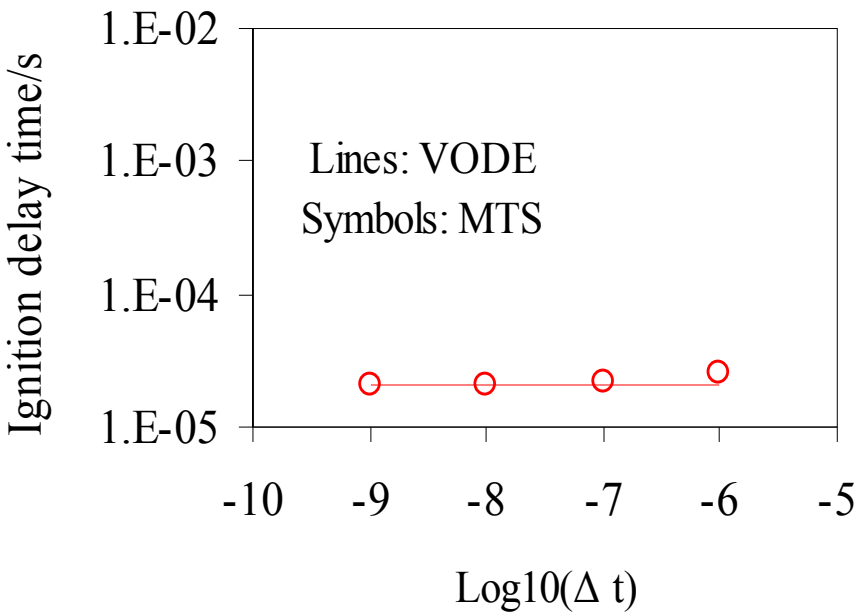


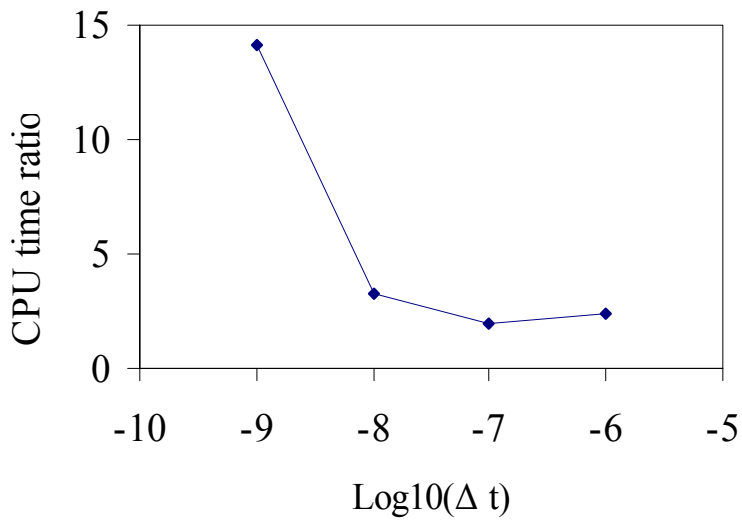
Validation of DMS Method (Hydrogen)



Homogeneous Ignition of Hydrogen with Air

No.	Output Time Step(s)	Initial pressure (atm)	Initial Temp. (K)	Out Time	RTOL	ATOL	CPU Time (s)	
							VODE	MTS
1	1.0E-6	1.0	1200	5.0E-4	1.0E-4	1.0E-13	0.28	0.13
2	1.0E-7	1.0	1200	5.0E-4	1.0E-4	1.0E-13	2.58	1.31
3	1.0E-8	1.0	1200	5.0E-4	1.0E-4	1.0E-13	24.9	7.56
4	1.0E-9	1.0	1200	5.0E-4	1.0E-4	1.0E-13	260	18.4





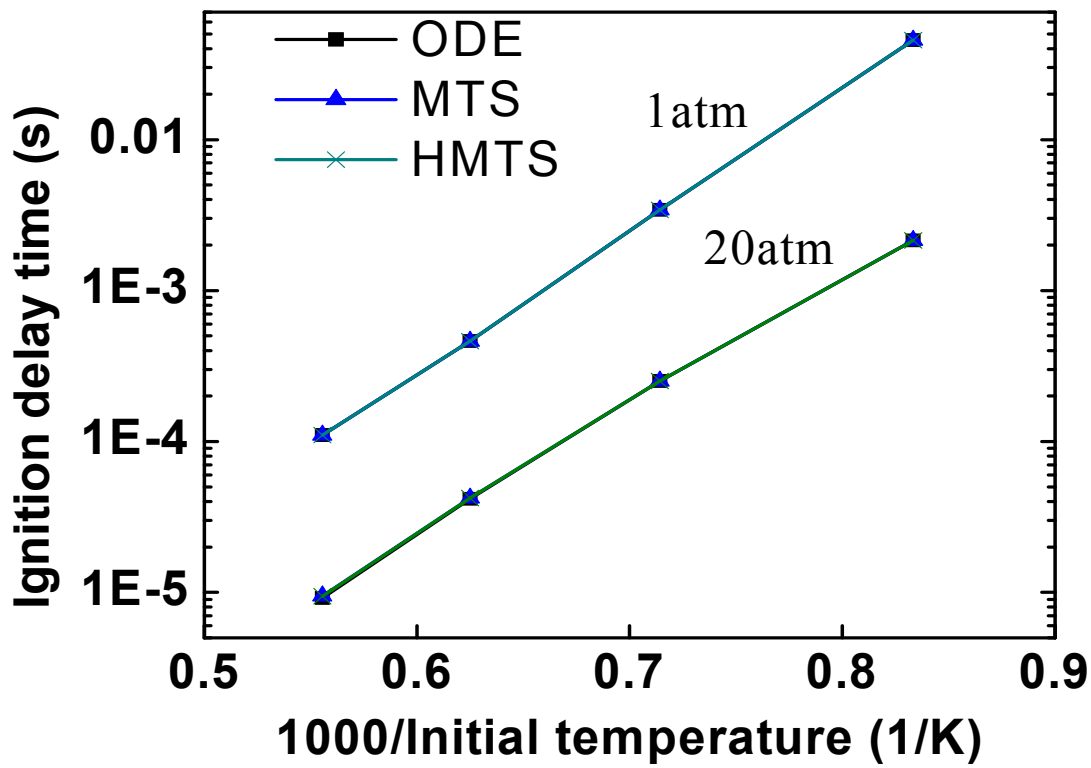
- **Reduces computation time by a factor of 2 to 15**

Homogeneous Ignition-CH_4/Air

Methane/Air

GRI-MECH 3.0, 53 species, 325 reactions (http://www.me.berkeley.edu/gri_mech)

- MTS considers all of the dynamic time scale in the solution method.
- Suppose one does not really have interest in the short time scale exact behavior?
- Ignore computing these results and only concentrate on larger dynamic time scale results-> The Hybrid-MTS (HMTS) method.



Ignition delay time comparison for different pressures

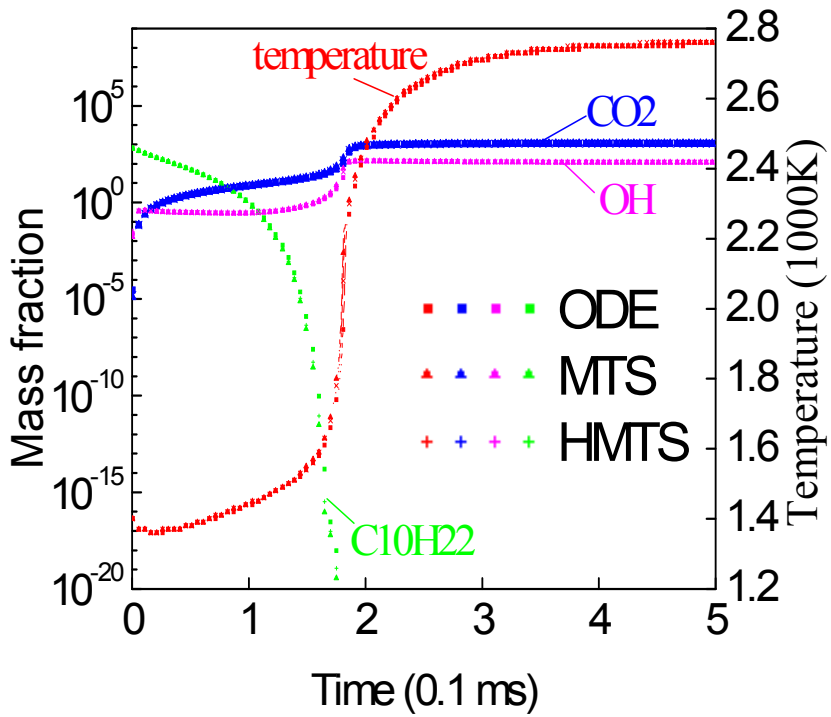
12~20 times faster

X. Gou, W. Sun, Z. Chen and Y. Ju, A Dynamic Multi-Timescale Method for Combustion Modeling with Detailed and Reduced Chemical Kinetic Mechanisms, submitted to Combustion and Flame, 2009

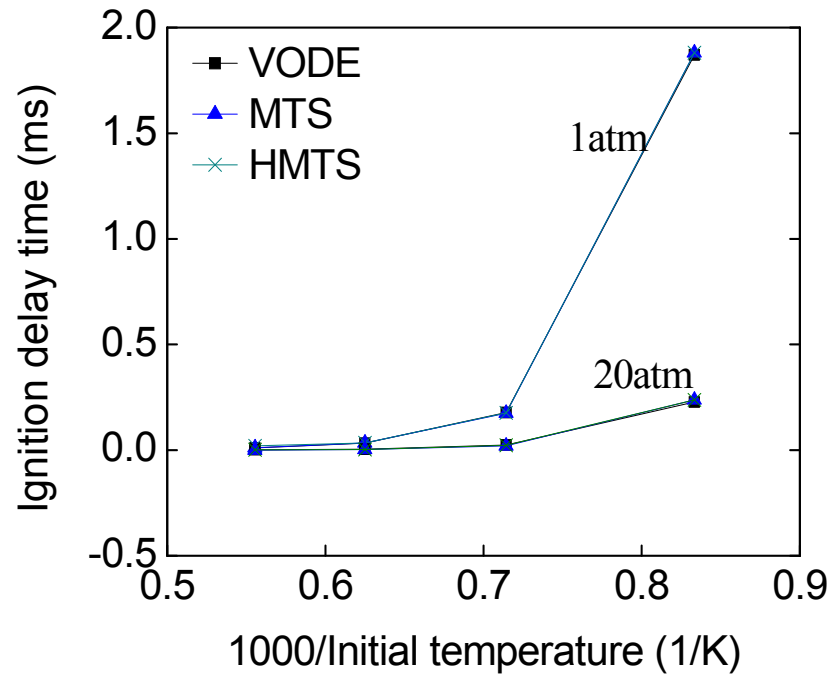
Validation by Homogeneous Ignition

n-decane/Air 121 species (M. Chaos, IJCK,2007)

Ignition in homogeneous mixture

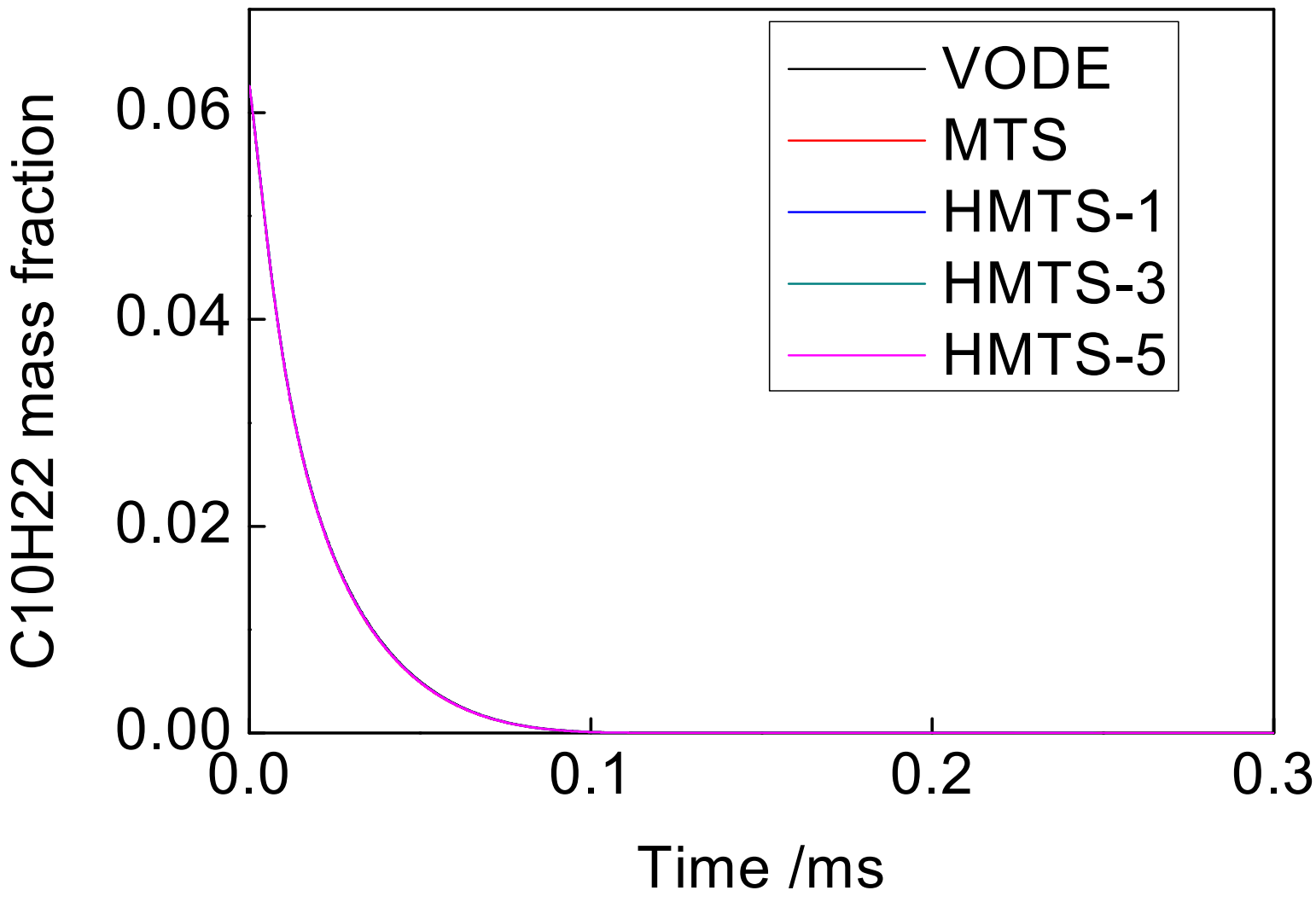


Temperature and species profiles



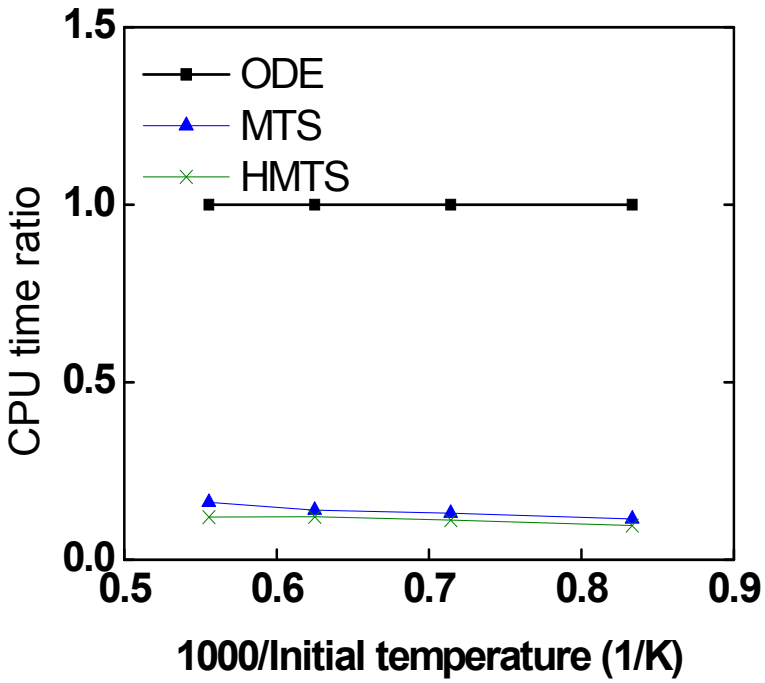
Ignition delay time for n-decane-air

Validation of MTS and HMTS

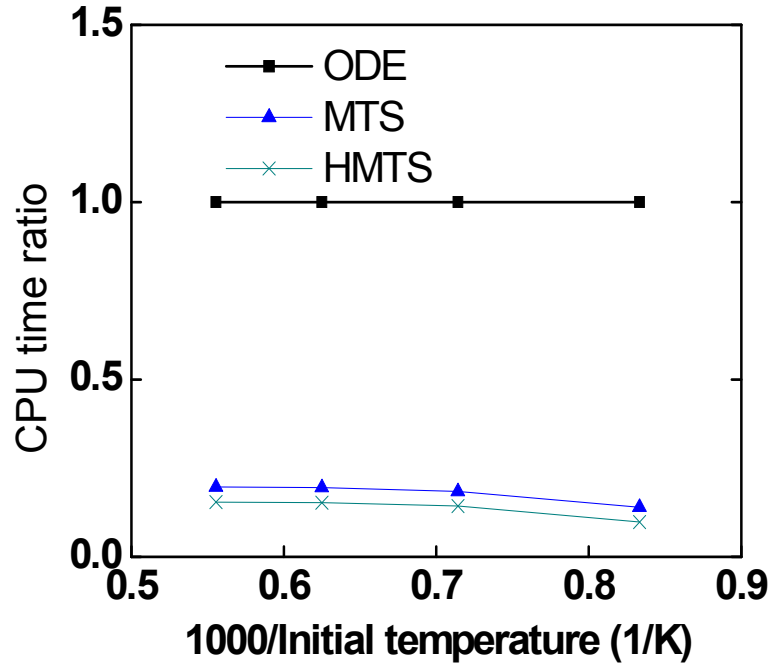


Computation Efficiency: Comparison with ODE Solver

Normalized by the computation time of ODE solver



1atm



20atm

7~10 times faster

Concluding Remarks

- A rigorous experimental approach for flame speed measurement at high pressures has been developed.
- Hydrogen Burning Rate has a positive dependence on pressure up to 15 atm, but a negative dependence at higher pressures.
- No models presently in the literature reproduce measured burning rates for hydrogen over all equivalence ratios and at reduced flame temperatures.
- Consideration of recent elementary kinetic understanding has permitted model updating of Li et al. (2007) syngas model such that predictions of burning rates at reduced flame temperatures and high pressures are much improved while predictions of data from other kinetic venues remains.
- Models are likely to continue to evolve through advances in theoretical understanding of hydroperoxyl radical reactions.
- Uncertainties in individual reaction parameters may still result in quantitative uncertainties in reaction model predictions of systems observations.
- Methods that consider both A factor and non-Arrhenius temperature parameters effects will be needed to achieve more universal optimization of model predictions against experiments.
- Experimental data that quantify H_2O_2, other radical species in both homogenous kinetic experiments and flames are needed to further constrain model validations.
- A dynamic multiscale model solver approach for handling stiff systems has been developed to reduce computational time by about one order of magnitude.
- Hybrid multiscale computational methods combined with evolving path analysis methods for skeletal model development should lead to major improvements in computational efficiencies for reactive flows.

Thank you.

Questions?