Experiments and Reaction Models of Fundamental Combustion Properties (2)

Hai Wang

B. Sirjean, D. A. Sheen, E. Dames,
X. Q. You, F. N. Egolfopoulos

University of Southern California

Summary of task status

- **Toward a predictive transport theory of *n*-alkanes**

  Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos F.N. "Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion," *Proceedings of the Combustion Institute,* in press (2008).

  Wang, H. "Transport properties of small spherical particles," *Annals of the New York Academy of Science*, Interdisciplinary Transport Phenomena V: Fluid, Thermal, Biological, Materials & Space Sciences, S. S. Sadhal Ed., in press (2008).

- **Uncertainty quantification, propagation, and minimization**

  Sheen, D. A., You, X., Wang, H., Løvås, T. "Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion," *Proceedings of the Combustion Institute*, in press (2008).

- **Collaborative development of a Jet Surrogate Fuel (JetSurF) combustion model**

  You, X.Q., Egolfopoulos F.N., Wang, H. "Detailed and simplified kinetic models for *n*-dodecane oxidation: the role of fuel cracking in aliphatic hydrocarbon combustion," *Proceedings of the Combustion Institute,* in press (2008).

  Smallbone, A., Liu, W., Law, C.-K., You, X., Wang, H. "Experiment and modeling study of laminar flame speed and non-premixed counterflow ignition of *n*-heptane," *Proceedings of the Combustion Institute,* in press (2008).

  Web Release: B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, **F. N. Egolfopoulos**, **H. Wang**, S. S. Vasu, D. F. Davidson, **R. K. Hanson**, **H. Pitsch**, **C. T. Bowman**, A. Kelley, **C. K. Law**, **W. Tsang**, **N. P. Cernansky**, **D. L. Miller**, **A. Violi**, **R. P. Lindstedt**, *A high-temperature chemical kinetic model of n-alkane oxidation*, JetSurF version 0.2, September 08, 2008 (http://melchior.usc.edu/JetSurF/Version0_2/Index.html).

- **Other work**

  Cathey, C., Cain, J., Wang, H., Gundersen, M. A., Carter, C., Ryan, M. "OH production by transient plasma and mechanism of flame ignition and propagation in quiescent methane-air mixtures," *Combustion and Flame*, 154, pp. 715-727 (2008).

Summary of task status

- **Toward a predictive transport theory of *n*-alkanes**

  Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos F.N. "Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion," *Proceedings of the Combustion Institute,* in press (2008).

  Wang, H. "Transport properties of small spherical particles," *Annals of the New York Academy of Science*, Interdisciplinary Transport Phenomena V: Fluid, Thermal, Biological, Materials & Space Sciences, S. S. Sadhal Ed., in press (2008).

- **Uncertainty quantification, propagation, and minimization**

  Sheen, D. A., You, X., Wang, H., Løvås, T. "Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion," *Proceedings of the Combustion Institute*, in press (2008).

- **Collaborative development of a Jet Surrogate Fuel (JetSurF) combustion model**

  You, X.Q., Egolfopoulos F.N., Wang, H. "Detailed and simplified kinetic models for *n*-dodecane oxidation: the role of fuel cracking in aliphatic hydrocarbon combustion," *Proceedings of the Combustion Institute,* in press (2008).

  Smallbone, A., Liu, W., Law, C.-K., You, X., Wang, H. "Experiment and modeling study of laminar flame speed and non-premixed counterflow ignition of *n*-heptane," *Proceedings of the Combustion Institute,* in press (2008).

  Web Release: B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, **F. N. Egolfopoulos**, **H. Wang**, S. S. Vasu, D. F. Davidson, **R. K. Hanson**, **H. Pitsch**, **C. T. Bowman**, A. Kelley, **C. K. Law**, **W. Tsang**, **N. P. Cernansky**, **D. L. Miller**, **A. Violi**, **R. P. Lindstedt**, *A high-temperature chemical kinetic model of n-alkane oxidation*, JetSurF version 0.2, September 08, 2008 (**http://melchior.usc.edu/JetSurF/Version0_2/Index.html**).

- **Other work**

  Cathey, C., Cain, J., Wang, H., Gundersen, M. A., Carter, C., Ryan, M. "OH production by transient plasma and mechanism of flame ignition and propagation in quiescent methane-air mixtures," *Combustion and Flame*, 154, pp. 715-727 (2008).

JetSurF – Phase 1

- **High-temperature** chemistry only.
- Focus on kinetic/thermodynamic/transport parameter **consistency**.
- All *n*-alkanes up to ***n*-dodecane**.
- **Work-in-progress**: no parameter tuning or optimization.
- **Web releases** as the effort evolves (**JetSurF 0.2** released today!)
- Close interactions among experimentalists, modelers and theoreticians – a truly **multidisciplinary** approach.

JetSurF – Phase 1

JetSurF - A Jet Surrogate Fuel Model - Windows Internet Explorer

http://melchior.usc.edu/JetSurF/

JetSurF - A Jet Surrogate Fuel Model

JetSurF – A Jet Surrogate Fuel Model

JetSurF is a detailed chemical reaction model for the combustion of jet-fuel surrogate. The model is being developed through a multi-university research collaboration and is funded by the **Air Force Office of Scientific Research**. Project participants include

F. N. Egolfopoulos, Hai Wang	*University of Southern California*
R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch	*Stanford University*
C. K. Law	*Princeton University*
N. P. Cernansky, D. L. Miller	*Drexel University*
W. Tsang	*National Institute of Standards and Technology*
R. P. Lindstedt	*Imperial College, London*
A. Violi	*University of Michigan*

Current Release: **JetSurF (Version 0.2)** *(Release Date: September 08, 2008)*

© 2008- JetSurF

JetSurF Version 0.2

JetSurF (Version 0 - Windows Internet Explorer

http://melchior.usc.edu/JetSurF/Version0_2/howtocit

Live Search

JetSurF (Version 0

Page Tools

JetSurF (Version 0.2)

Release date: September 08, 2008

Main page | JetSurF 0.2 download | Performance | How to cite

How to Cite JetSurF 0.2:

B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S. S. Vasu, D. F. Davidson, R. K. Hanson, H. Pitsch, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, A high-temperature chemical kinetic model of *n*-alkane oxidation, JetSurF version 0.2, September 08, 2008 (http://melchior.usc.edu/JetSurF/Version0_2/Index.html).

Note:

Detailed reaction model development is inherently a work in progress. The current release is for the purpose of discussion and evaluation. Although the model predicts a large body of experimental data, it should be used with caution. The release is meant to be used for modeling the pyrolysis and oxidation of *n*-alkane (up to *n*-dodecane) at high temperatures only.

Internet 100%

JetSurf 0.2 – Highlights

- **194 species & 1459 reactions**
- **C_1-C_4 and some aromatics chemistry: USC Mech II**

  H. Wang, X. Q. You, A. V. Joshi, S. G. Davis, A. Laskin, F. N. Egolfopoulos & C. K. Law, USC Mech Version II. *High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds.* http://ignis.usc.edu/USC_Mech_II.htm, May 2007.

- **Chemistry for *n*-pentane to *n*-dodecane**

Reaction type	Source and Method of Rate Estimation	Pressure fall-off
C-C bond fission in *n*-alkane	Back rate constant from $2C_2H_5 \rightarrow n\text{-}C_4H_{10}$ (k_∞)	No
H-abstraction by H, O, OH, O_2, and CH_3	Cohen's method. Used the rate constants of $C_3H_8 + X \rightarrow n\text{-}C_3H_7$ or $i\text{-}C_3H_7 + HX$	N/A
Mutual isomerization of alkyl radicals (1,4, 1,5 and 1,6 H-shift) C-C and C-H *beta*-scission in alkyl radicals	Tsang, Manion and co-workers.	Yes

- **12 step-4 species semi-empirical description of low-T chemistry**
- **Thermochemistry: group additivity (consistent with USC Mech II)**
- **Transport properties: empirical (to be discussed)**

JetSurF – Performance we know

Compound	Flame speed	Ignition delay	Species profiles: Shock tube	Species profiles: Burner stab. flame	Species profiles: Flow reactor	Species profiles: Jet stirred reactor
n-C_5H_{12}	**5** (1 – 10)	**3** (1.7 – 3.5)				
n-C_6H_{14}	**2** (1)	**3** (1.8 – 3.4)				
n-C_7H_{16}	**5** (0.5 – 2)	**9** (1 – 4)	**3** (2)			
n-C_8H_{18}	**1** (1)	**3** (2 – 3.6)				
n-C_9H_{20}	**1** (1)	**3** (2 – 3.5)				
n-$C_{10}H_{22}$	**1** (1)	**4** (1 – 13)	**3** (2)			
n-$C_{11}H_{24}$						
n-$C_{12}H_{26}$	**1** (1)	**2** (20)			**1** (1)	**2** (1 & 8)
CH_4	**1** (1)					
C_2H_6	**1** (1)					
C_3H_8	**1** (1)	**4** (3 – 15)				
n-C_4H_{10}	**1** (1)					
H_2	**6** (1 – 20)	**11** (1 – 85)	**2** (0.8 – 1.1)		**4** (0.6 – 16)	
H_2/CO or CO/H_2O	**5** (1)	**2** (1 – 2)	**4** (1 – 400)		**4** (1 – 10)	
C_2H_2	**1** (1)	**4** (0.2 – 2)		**1** (0.12)		
C_2H_4	**3** (1 – 5)	**6** (0.7 – 3)		**2** (0.03, 1)	**12** (1 – 10)	
C_2H_6	**1** (1)					
p-C_3H_4	**1** (1)	**3** (3.5)				
a-C_3H_4	**1** (1)	**3** (2)				
C_3H_6	**1** (1)	**5** (1-4)				
1,3-C_4H_6	**1** (1)					
1-C_4H_8	**1** (1)					
# Data Sets	**41**	**65**	**12**	**3**	**19**	**2**

142

JetSurF – Performance we know

JetSurF (Version 0 - Windows Internet Explorer

http://melchior.usc.edu/JetSurF/Version0_2/Performance.html

JetSurF (Version 0.2)

Release date: September 08, 2008

Main page | JetSurF 0.2 download | Performance | How to cite

Performance That We Know:

Validation tests for the base model can be found at the USC-Mech II website:

- Ignition Delays
- Species Profiles in Shock-Tube Oxidation
- Laminar Flame Speeds
- Flow Reactor
- Burner Stabilized Flames

These tests include the oxidation of H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, pC_3H_4 (propyne), aC_3H_4 (allene), C_3H_6, C_3H_8, 1,3-C_4H_6 (1,3-butadiene), 1-C_4H_8 (1-butene), n-C_4H_{10} (n-butane).

For higher-hydrocarbons, validation tests include

- Laminar flame speeds

  n-dodecane-air mixtures, $p = 1$ atm, $T_u = 403$ K.
  You, Egolfopoulos & Wang (2008)

  C_kH_{2k+2} ($5 \le k \le 10$)-air mixtures, $\phi = 0.7$ to 1.5, $p = 1$ atm, $T_u = 353$. K for $5 \le k \le 8$ and 403 K for $k = 9$ & 10.
  Egolfopoulos et al. unpublished (2008)

  n-pentane, n-hexane & n-heptane-air mixtures, $p = 1$ atm, $T_u = 298$ K.
  Davis & Law (1998).

  n-Heptane-air mixtures, $p = 0.5$ to 2 atm, $T_u = 350$ K.
  Smallbone et al. (2008).

  n-Pentane-air mixtures, $p = 1, 2, 5$ & 10 atm, $T_u = 353$ K.
  Kelley & Law. unpublished (2008).

- Ignition delay times behind reflected shock waves

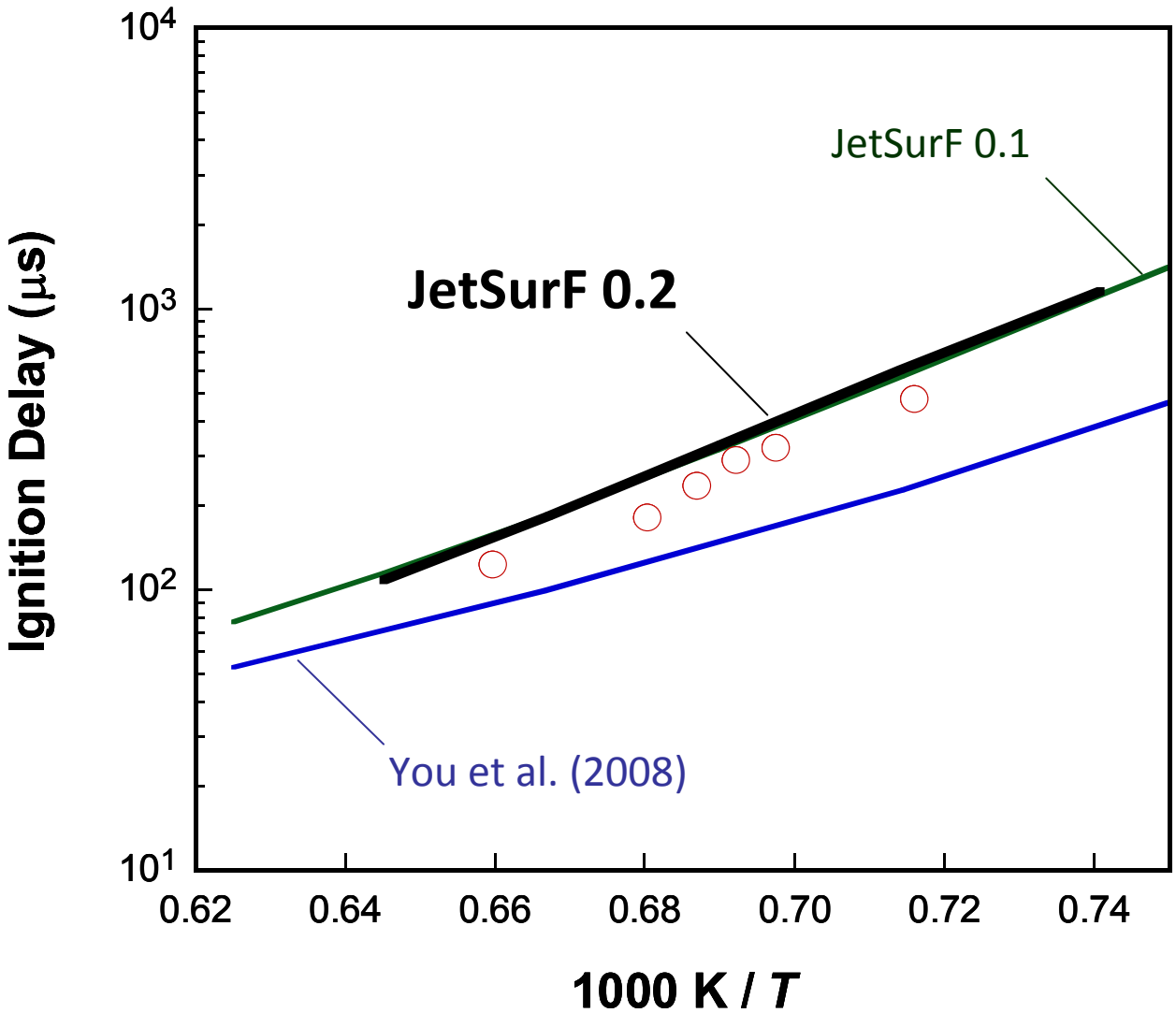
  n-dodecane-oxygen-nitrogen, $p_5 = 20$ atm.
  Vasu, Davidson, Hong, Vasudevan & Hanson (2008).

  n-decane-oxygen-argon and n-heptane-oxygen-argon mixtures, $1 \le p_5 \le 4$ atm.
  Horning, Davidson & Hanson (2002).

  n-decane-oxygen-argon mixtures, $1 \le p_5 \le 2$ atm.
  Smith, Simmie & Curran (2005).

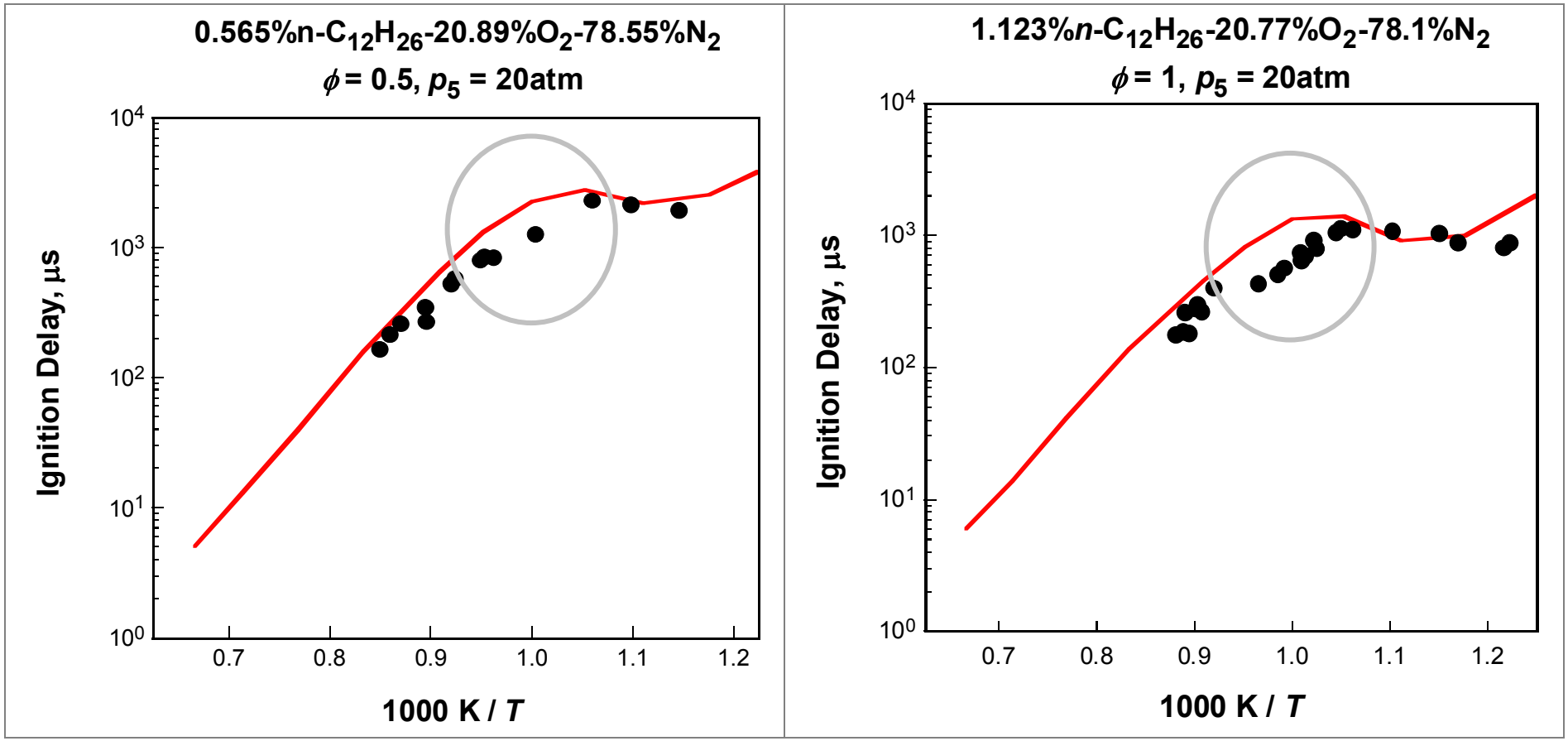
JetSurF – Examples

0.2%*n*-$C_{10}H_{22}$ - 3.1%O_2 in Ar, ϕ = 1, p_5 = 1.23 atm



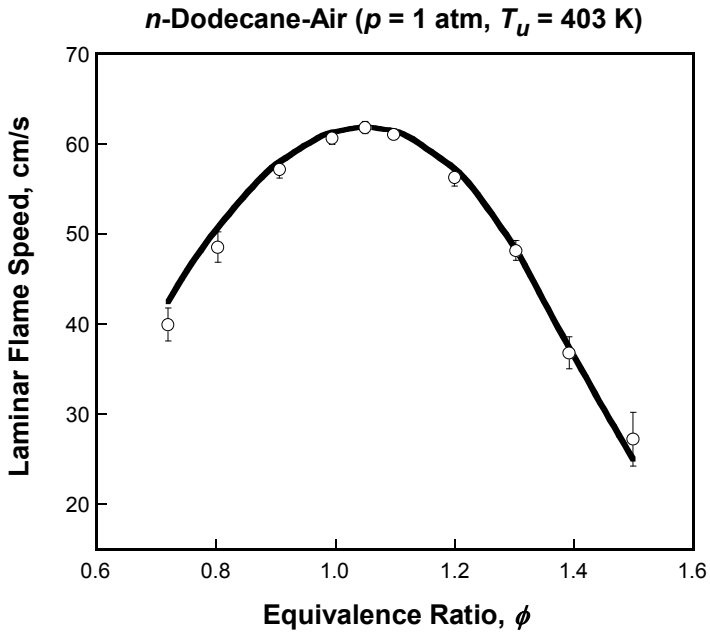
Data: D.C. Horning, D.F. Davidson, **R.F. Hanson** (2002)

JetSurF – Examples



Data: S.S. Vasu, D.F. Davidson, Z. Hong, V. Vasudevan, **R.K. Hanson** (2008).

JetSurF – Examples

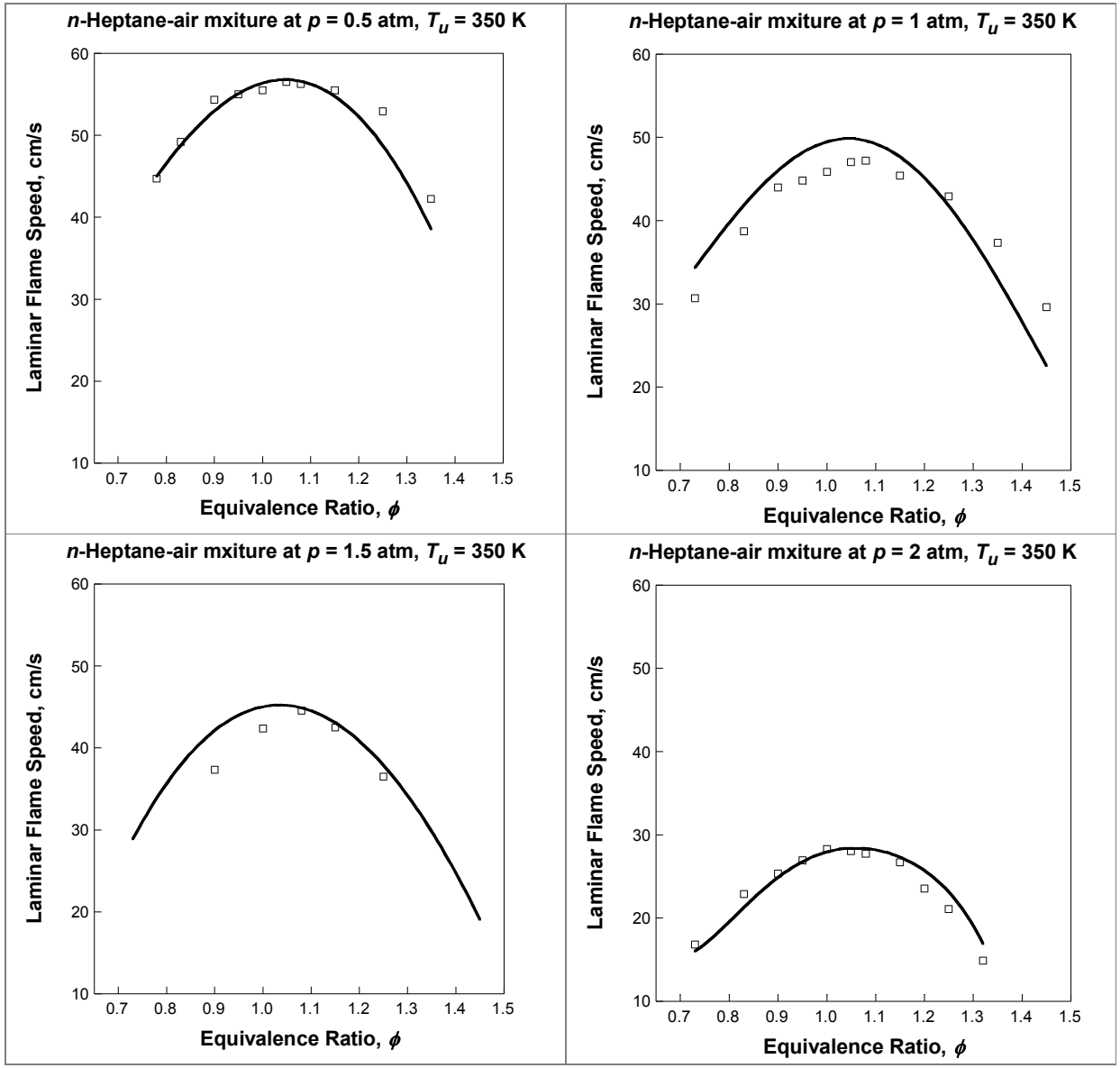


Data: X. You, **F. N Egolfopoulos**, H. Wang (2008)

Unpublished data not shown here.

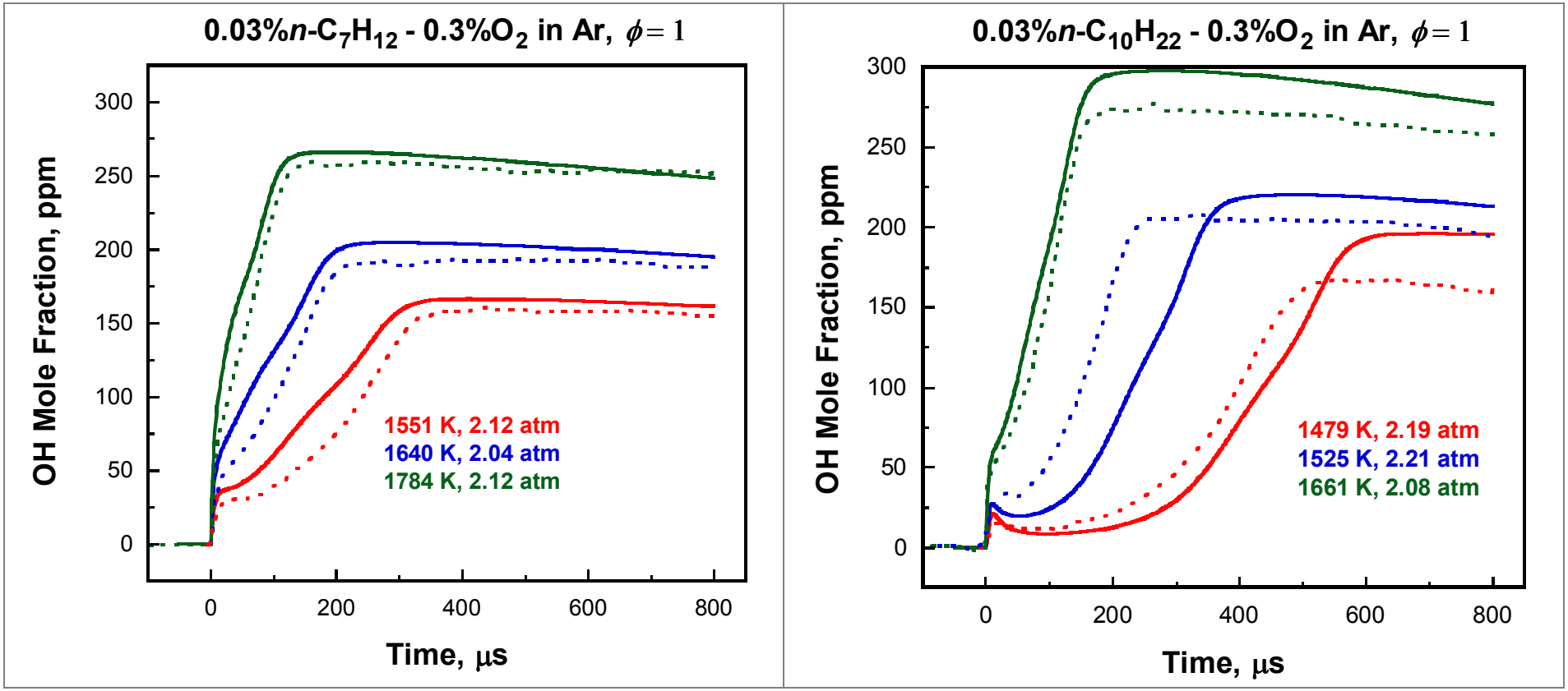
Data: **F. N Egolfopoulos**, unpublished (2008).

JetSurF – Examples



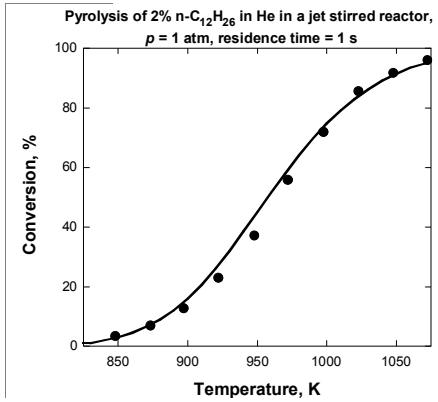
Data: Smallbone, A., Liu, W., **Law, C.-K.**, You, X., Wang, H. (2008)

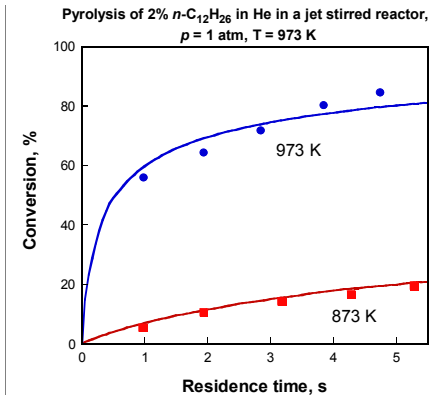
JetSurF – Examples

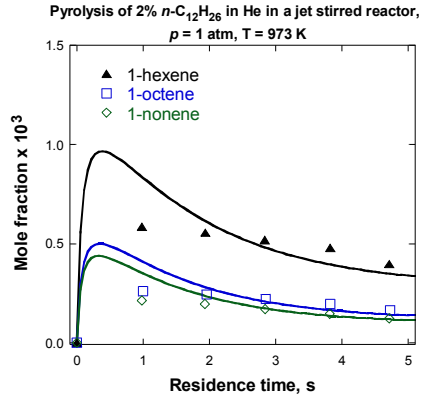


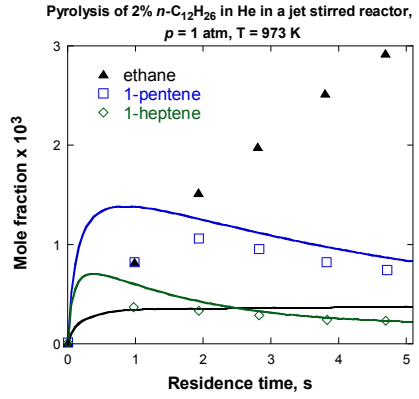
Data: D. F. Davidson, J. T. Herbon, D. C. Horning, **R. K. Hanson** (2001).

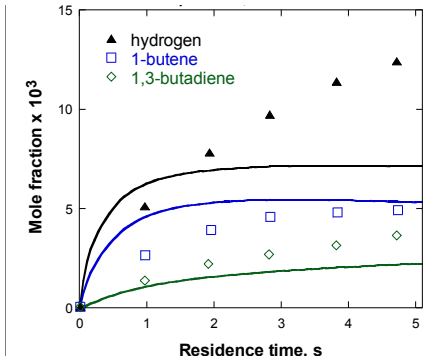
JetSurF – Examples

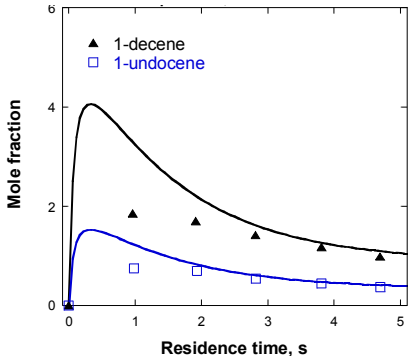


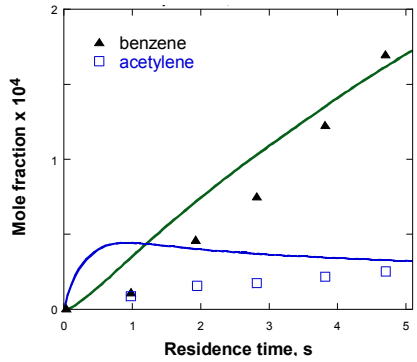


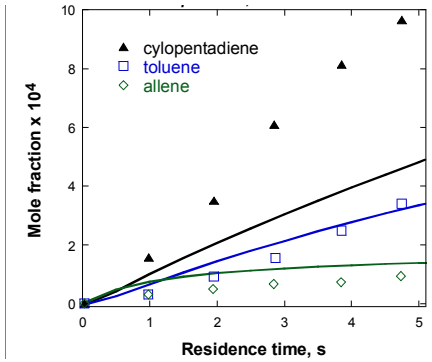


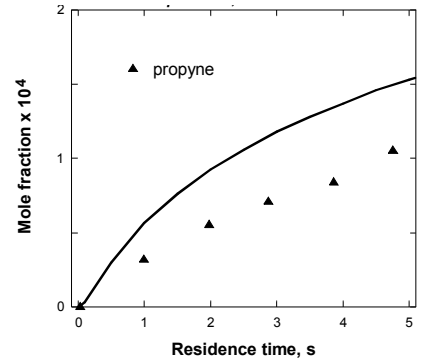


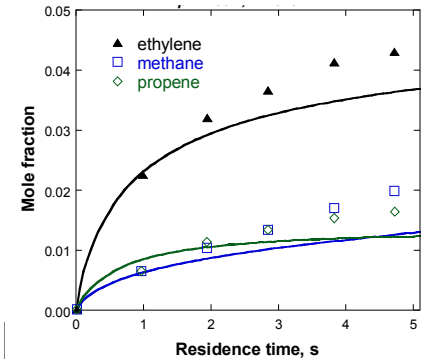






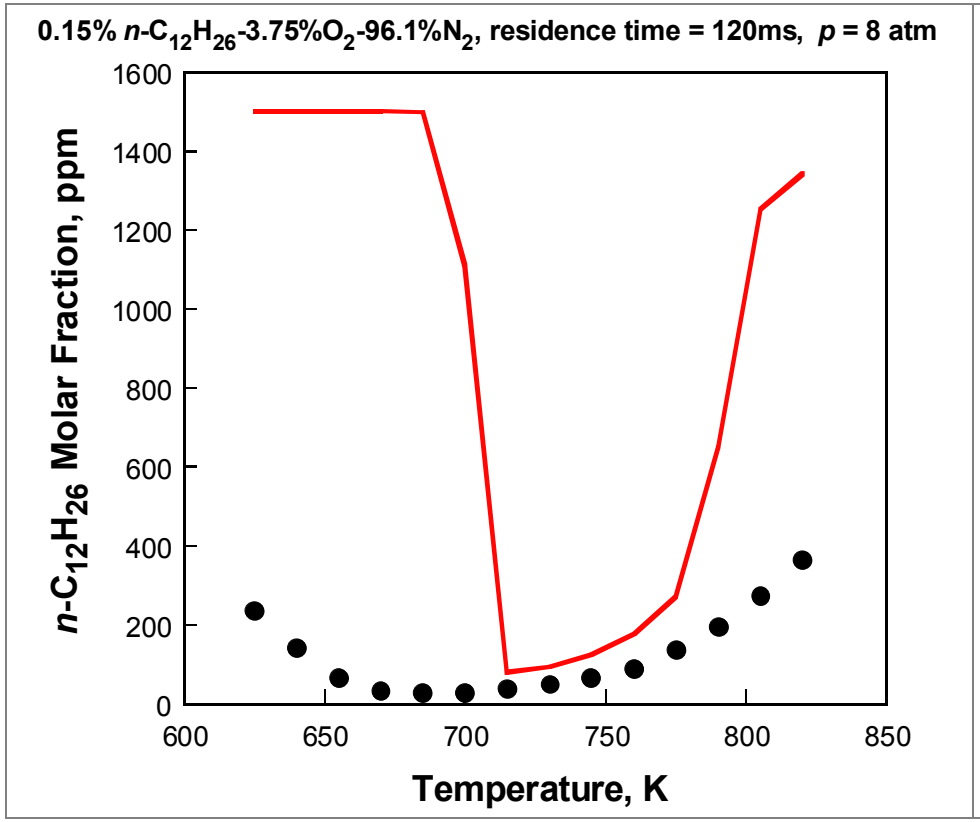


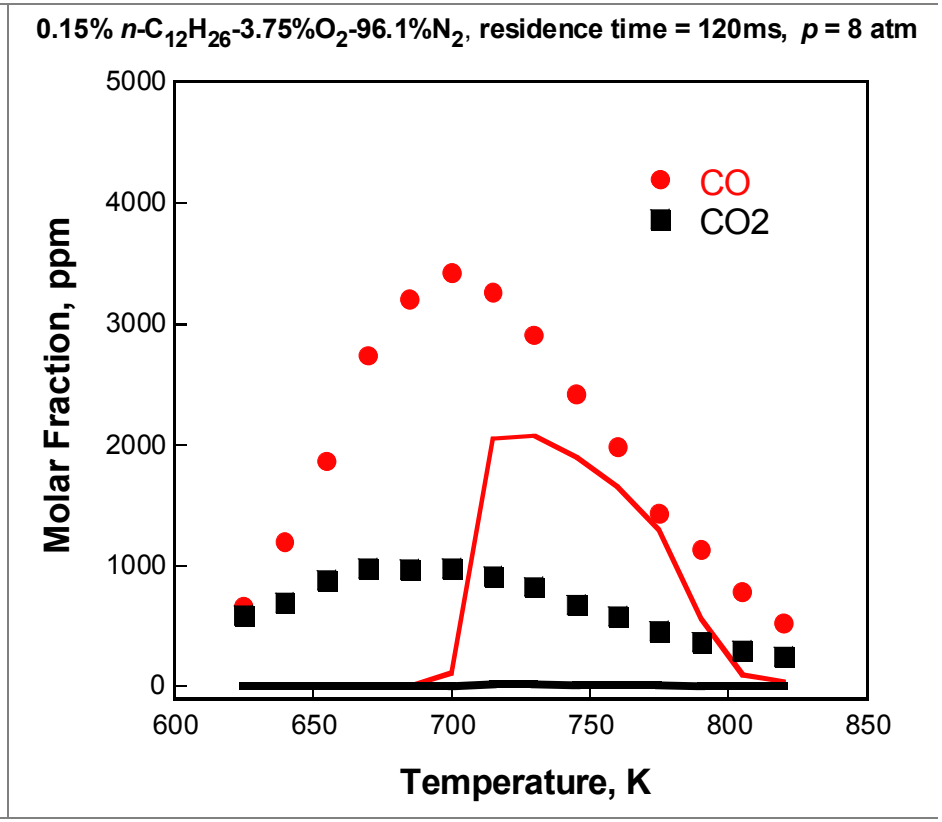




Data: O. Herbinet, P.M. Marquaire, **F. Battin-Leclerc**, R. Fournet (2007).

JetSurF – Examples





Data: M. S. Kurman, R. H. Natelson, **N. P. Cernansky, D. L. Miller** (2008).

JetSurF – version 0.2

- For T > 1000 K, *n*-alkane fragmentation is not rate limiting;
- Flame propagation rate and ignition delay insensitive to fragmentation chemistry;
- $C_{1\text{-}4}$ chemistry requires update (PrIMe effort);
- Need data for intermediate species (time evolution in shock tubes and flow reactors);
- Low temperature chemistry;
- Quantify model uncertainty.

Summary of task status

- **Toward a predictive transport theory of *n*-alkanes**

  Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos F.N. "Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion," *Proceedings of the Combustion Institute,* in press (2008).

  Wang, H. "Transport properties of small spherical particles," *Annals of the New York Academy of Science*, Interdisciplinary Transport Phenomena V: Fluid, Thermal, Biological, Materials & Space Sciences, S. S. Sadhal Ed., in press (2008).

- **Uncertainty quantification, propagation, and minimization**

  Sheen, D. A., You, X., Wang, H., Løvås, T. "Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion," *Proceedings of the Combustion Institute*, in press (2008).

- **Collaborative development of a Jet Surrogate Fuel (JetSurF) combustion model**

  You, X.Q., Egolfopoulos F.N., Wang, H. "Detailed and simplified kinetic models for *n*-dodecane oxidation: the role of fuel cracking in aliphatic hydrocarbon combustion," *Proceedings of the Combustion Institute,* in press (2008).

  Smallbone, A., Liu, W., Law, C.-K., You, X., Wang, H. "Experiment and modeling study of laminar flame speed and non-premixed counterflow ignition of *n*-heptane," *Proceedings of the Combustion Institute,* in press (2008).

  Web Release: B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, **F. N. Egolfopoulos**, **H. Wang**, S. S. Vasu, D. F. Davidson, **R. K. Hanson**, **H. Pitsch**, **C. T. Bowman**, A. Kelley, **C. K. Law**, **W. Tsang**, **N. P. Cernansky**, **D. L. Miller**, **A. Violi**, **R. P. Lindstedt**, *A high-temperature chemical kinetic model of n-alkane oxidation*, JetSurF version 0.2, September 08, 2008 (**http://melchior.usc.edu/JetSurF/Version0_2/Index.html**).

- **Other work**

  Cathey, C., Cain, J., Wang, H., Gundersen, M. A., Carter, C., Ryan, M. "OH production by transient plasma and mechanism of flame ignition and propagation in quiescent methane-air mixtures," *Combustion and Flame*, 154, pp. 715-727 (2008).

Transport Theory

- **Phase I: Empirical Estimation of L-J 12-6 potential parameters**

  Spherical potential
  Currently used in JetSurF
  Consistent but expected to be inaccurate

- **Phase II: Gas-kinetic theory analysis and analytical expressions to fuel diffusivity (ongoing, in collaboration with Manion and Violi)**

  Non-spherical potential
  Shape effect

Transport Theory - Empirical

- **Method of corresponding state with liquid properties (Mansoori et al. 1980).**

- **This work: the correlations of corresponding states of Tee, Gotoh & Stewart**

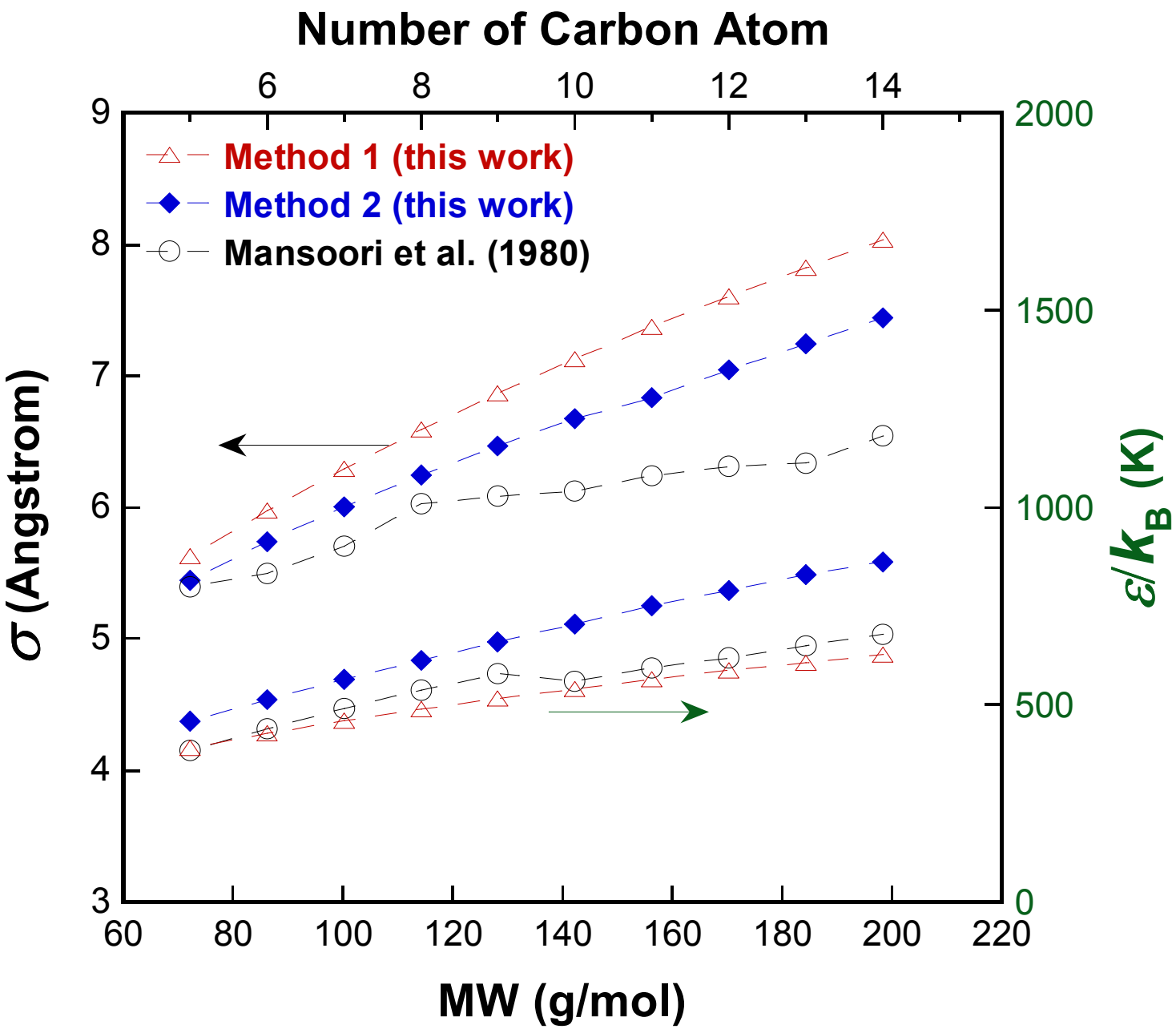
Method used for aromatics transport properties (Wang & Frenklach 1994)
Chapman-Enskog theory with spherical potential
L-J 12-6 parameters estimated from critical parameters

$$\sigma\left(\frac{P_c}{T_c}\right)^{1/3} = a_\sigma - b_\sigma\omega \qquad \frac{\varepsilon}{k_B T_c} = a_\varepsilon + b_\varepsilon\omega$$

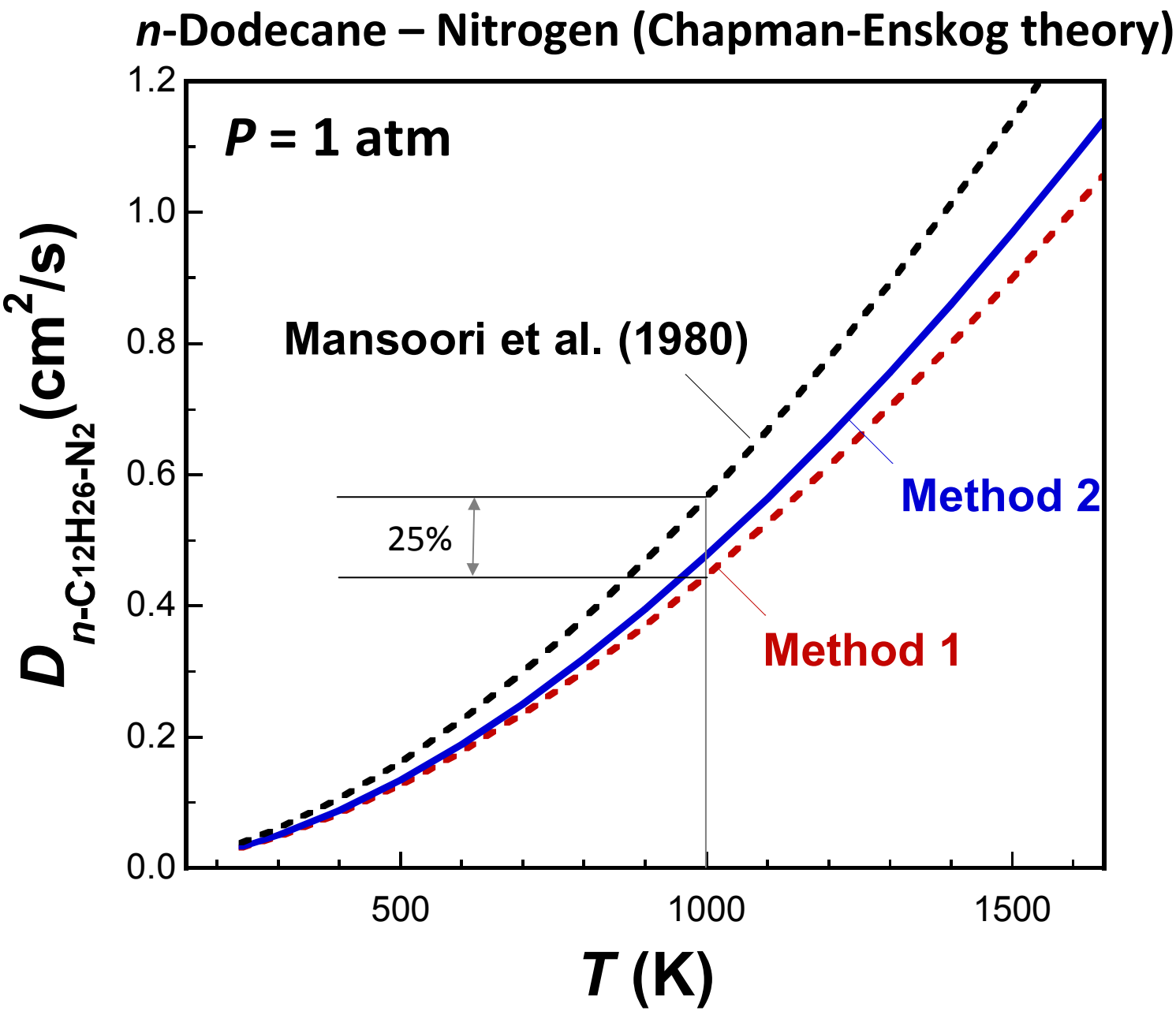
$$\omega = \frac{-\ln(P_c) - 5.93 + 6.10\theta^{-1} + 1.29\ln\theta - 0.17\theta^6}{15.25 - 15.69\theta^{-1} - 13.47\ln\theta + 0.44\theta^6} \qquad (\theta = T_b/T_c)$$

	a_σ	b_σ	a_ε	b_ε	Comments
Method 1:	2.3511	0.0874	0.7915	0.1693	all gases considered
Method 2:	2.3511	0.3955	0.8063	0.6802	hydrocarbon only

Transport Theory - Empirical

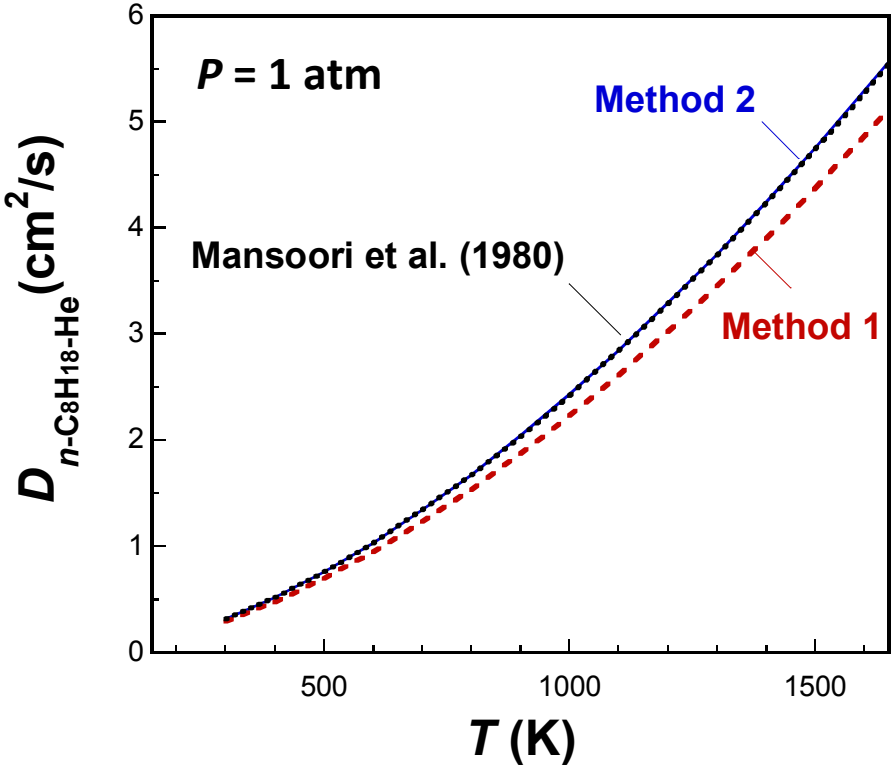


Transport Theory - Empirical

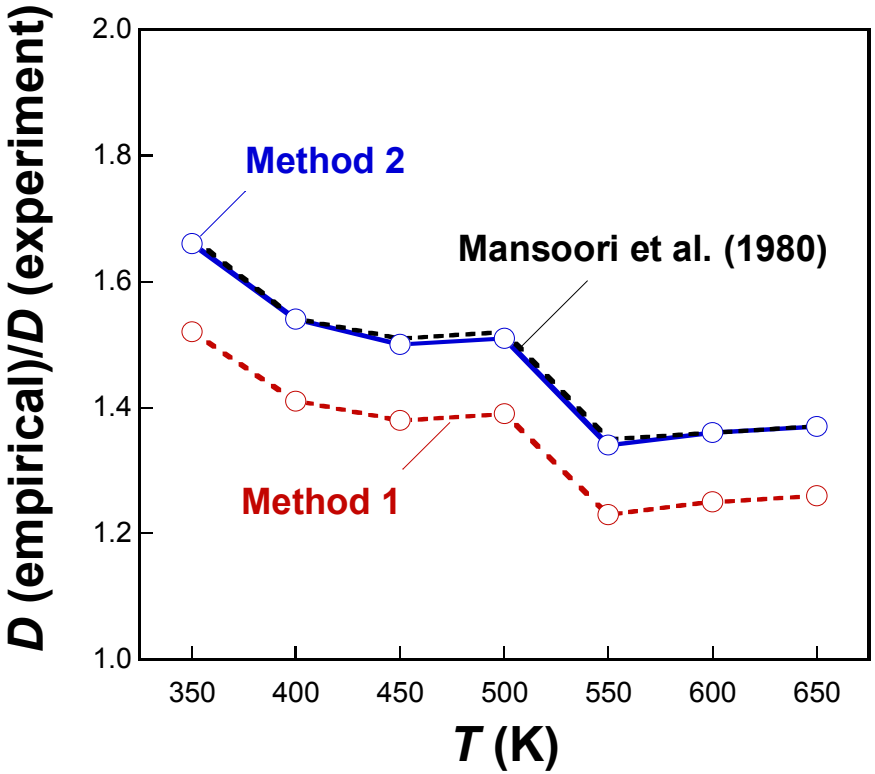


Transport Theory - Empirical

***n*-Octane – Helium**
Chapman-Enskog theory



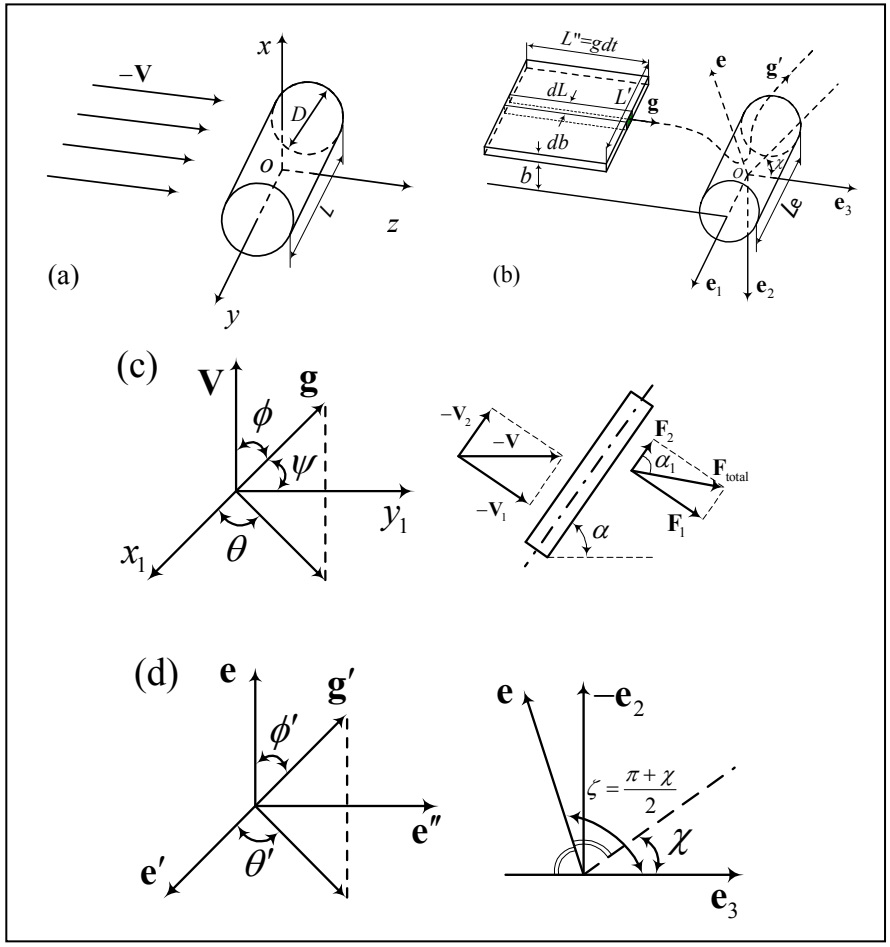
Comparison with experiment



Data: J. A. Manion, W. S. McGivern (2008)

Transport Theory - Analytical

A non-spherical, stick model beyond Chapman-Enskog (Li & Wang, unpublished)



Drag on a stick:

$$F_{s,\text{total}} = \frac{1}{2}\sqrt{\left(1+5\sin^2\alpha/4\right)2\pi m_r kT}\,NLDV\Omega_s^{(1,1)*}$$

Binary diffusivity: stick in a gas

$$D_{12} = 2\sqrt{\frac{kT}{\left(1+5\sin^2\alpha/4\right)2\pi m_r}}\,\frac{1}{NLD\Omega_s^{(1,1)*}}$$

Collision integral

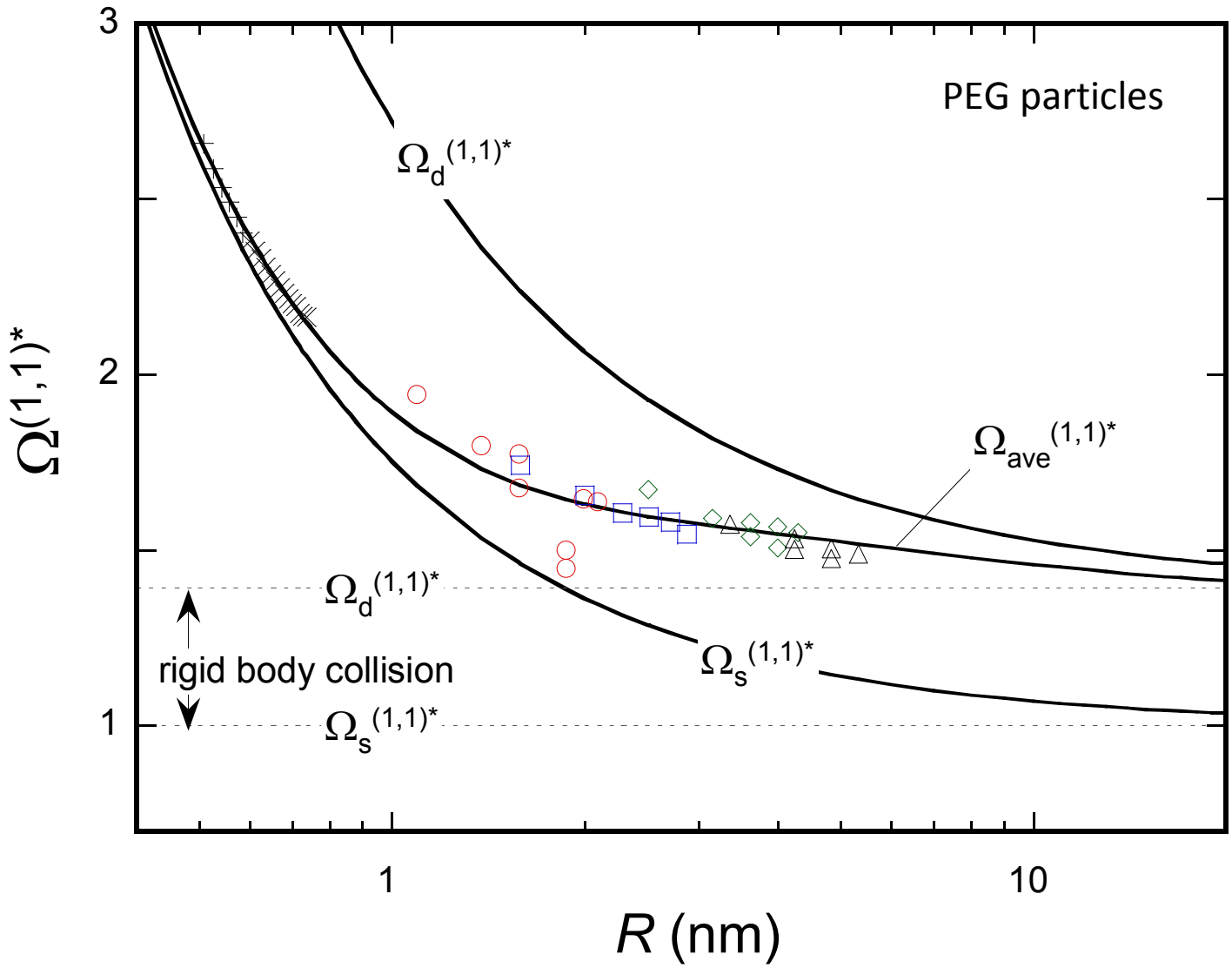
$$\Omega_s^{(1,1)*} = \frac{\int_0^\infty \gamma^5 \exp\left(-\gamma^2\right) Q_s(g)\,d\gamma}{LD}$$

Work-in-Progress:

- Develop and parameterize collision integral
- NIST experiments (J. Manion, NIST)
- MD simulation (A. Violi, U. Mich.)

Transport Theory – Spherical Particles

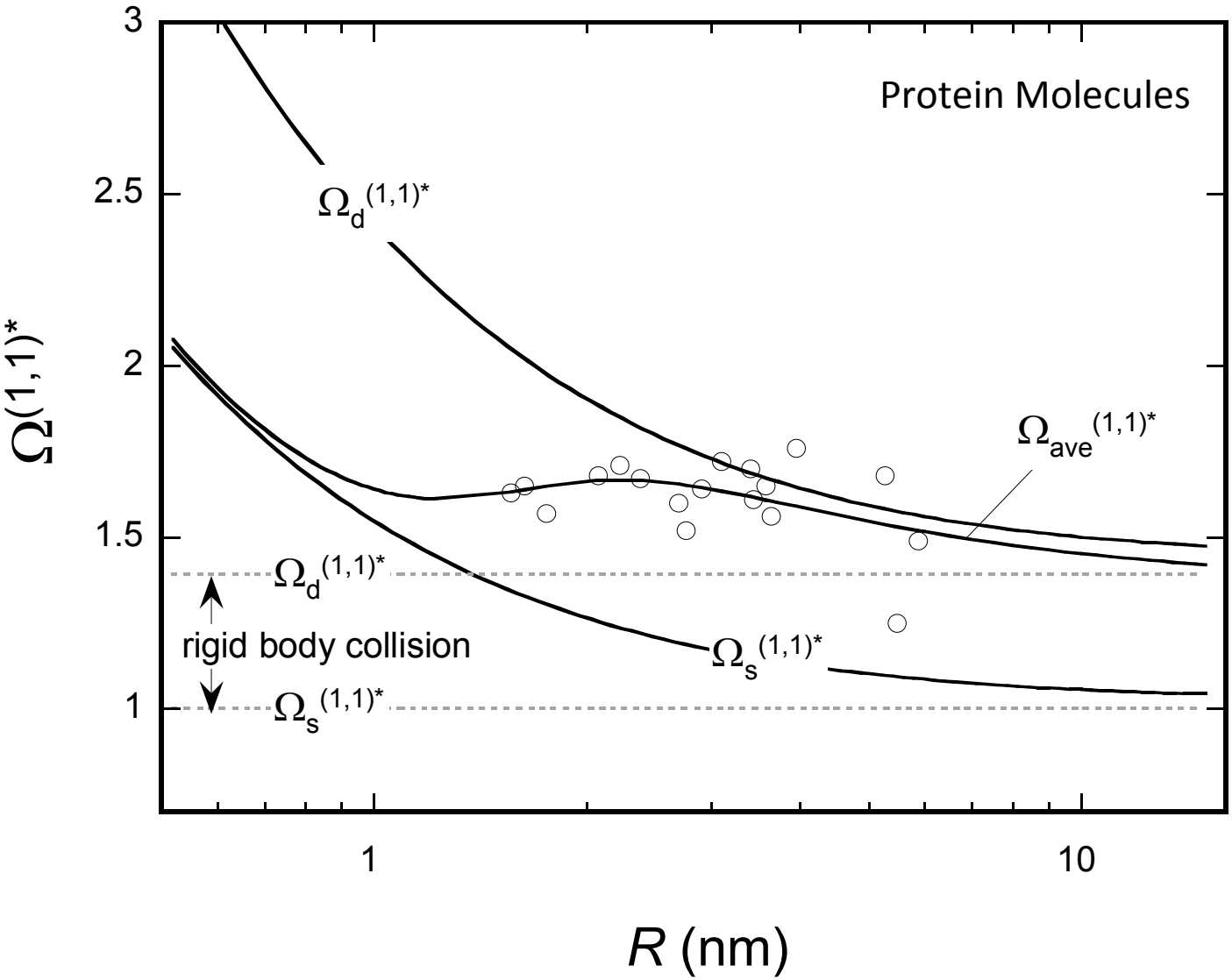
Transition from specular-elastic to diffuse scattering



Data: Fernández de la Mora (2002, 2003). Theory: Li and Wang, Phys. Rev. E (2003), Phys. Rev. Lett. (2005), Wang (2008)

Transport Theory – Spherical Particles

Transition from specular-elastic to diffuse scattering



Data: Kauffman (1996). Theory: Li and Wang, Phys. Rev. E (2003), Phys. Rev. Lett. (2005), Wang (2008)

Summary of task status

- **Toward a predictive transport theory of *n*-alkanes**

  Holley, A.T., You, X.Q., Dames, E., Wang, H., Egolfopoulos F.N. "Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion," *Proceedings of the Combustion Institute,* in press (2008).

  Wang, H. "Transport properties of small spherical particles," *Annals of the New York Academy of Science*, Interdisciplinary Transport Phenomena V: Fluid, Thermal, Biological, Materials & Space Sciences, S. S. Sadhal Ed., in press (2008).

- **Uncertainty quantification, propagation, and minimization**

  Sheen, D. A., You, X., Wang, H., Løvås, T. "Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion," *Proceedings of the Combustion Institute*, in press (2008).

- **Collaborative development of a Jet Surrogate Fuel (JetSurF) combustion model**

  You, X.Q., Egolfopoulos F.N., Wang, H. "Detailed and simplified kinetic models for *n*-dodecane oxidation: the role of fuel cracking in aliphatic hydrocarbon combustion," *Proceedings of the Combustion Institute,* in press (2008).

  Smallbone, A., Liu, W., Law, C.-K., You, X., Wang, H. "Experiment and modeling study of laminar flame speed and non-premixed counterflow ignition of *n*-heptane," *Proceedings of the Combustion Institute,* in press (2008).

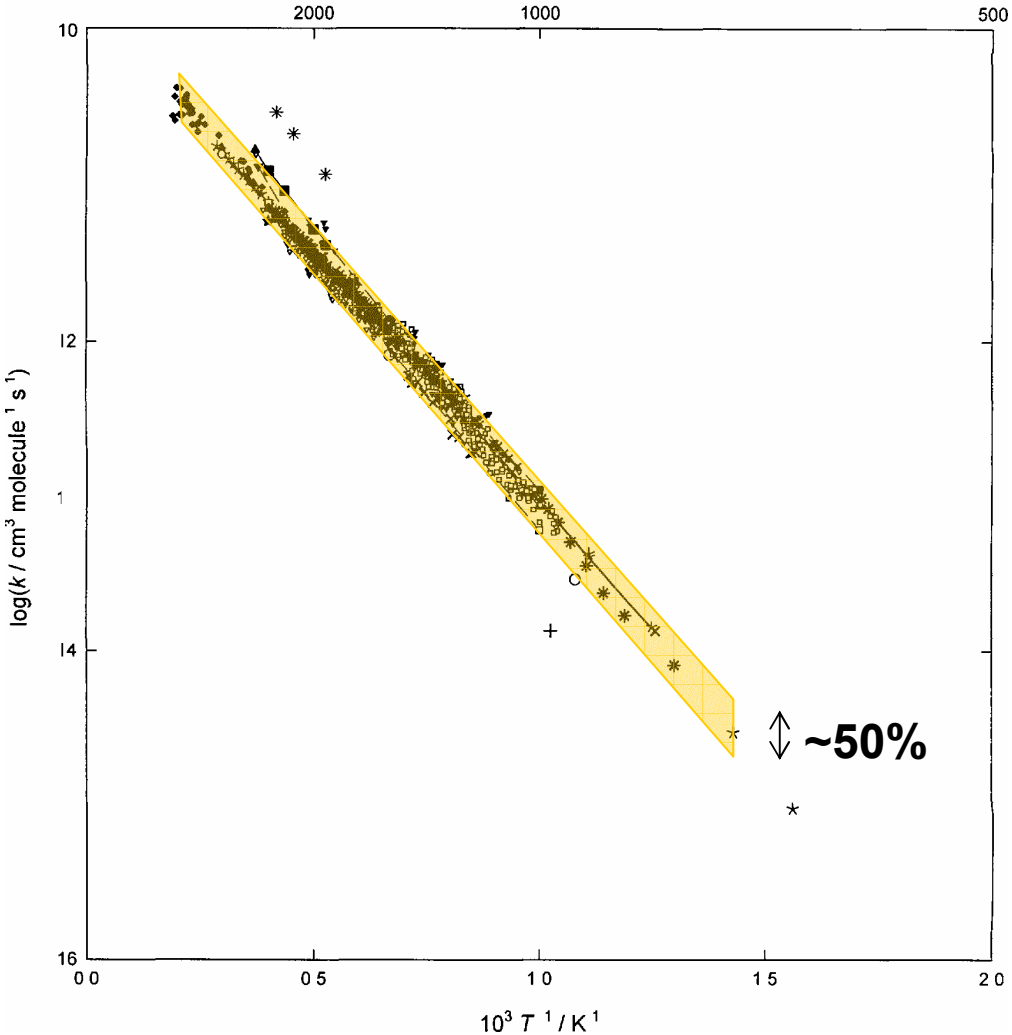
  Web Release: B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, **F. N. Egolfopoulos**, **H. Wang**, S. S. Vasu, D. F. Davidson, **R. K. Hanson**, **H. Pitsch**, **C. T. Bowman**, A. Kelley, **C. K. Law**, **W. Tsang**, **N. P. Cernansky**, **D. L. Miller**, **A. Violi**, **R. P. Lindstedt**, *A high-temperature chemical kinetic model of n-alkane oxidation*, JetSurF version 0.2, September 08, 2008 (**http://melchior.usc.edu/JetSurF/Version0_2/Index.html**).

- **Other work**

  Cathey, C., Cain, J., Wang, H., Gundersen, M. A., Carter, C., Ryan, M. "OH production by transient plasma and mechanism of flame ignition and propagation in quiescent methane-air mixtures," *Combustion and Flame*, 154, pp. 715-727 (2008).

Uncertainty quantification, propagation, and minimization

$H + O_2 \leftrightarrow OH + O$ (R1)



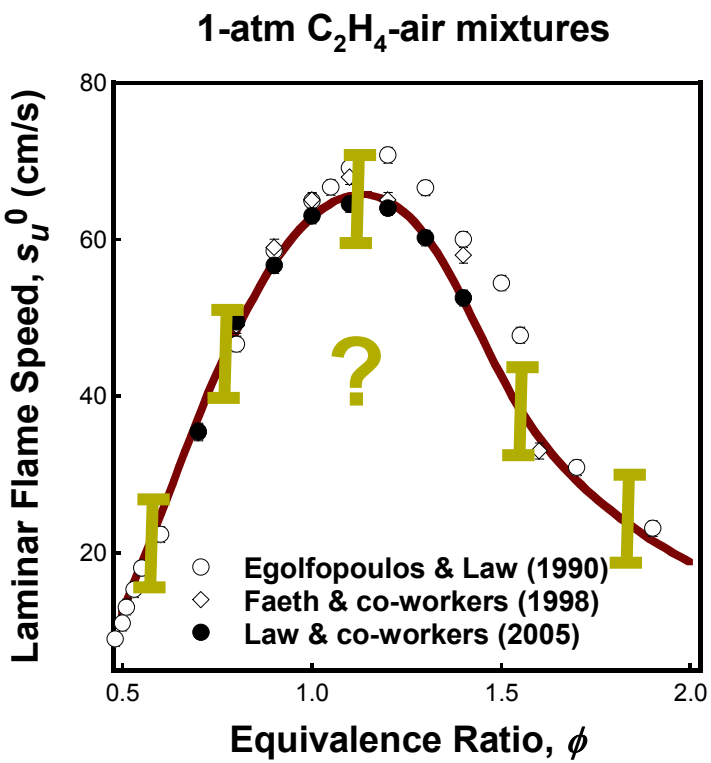
- Uncertainty factor ~1.25
- Logarithmic sensitivity coefficient = 0.24 (ethylene-air, ϕ = 1, p = 1 atm)

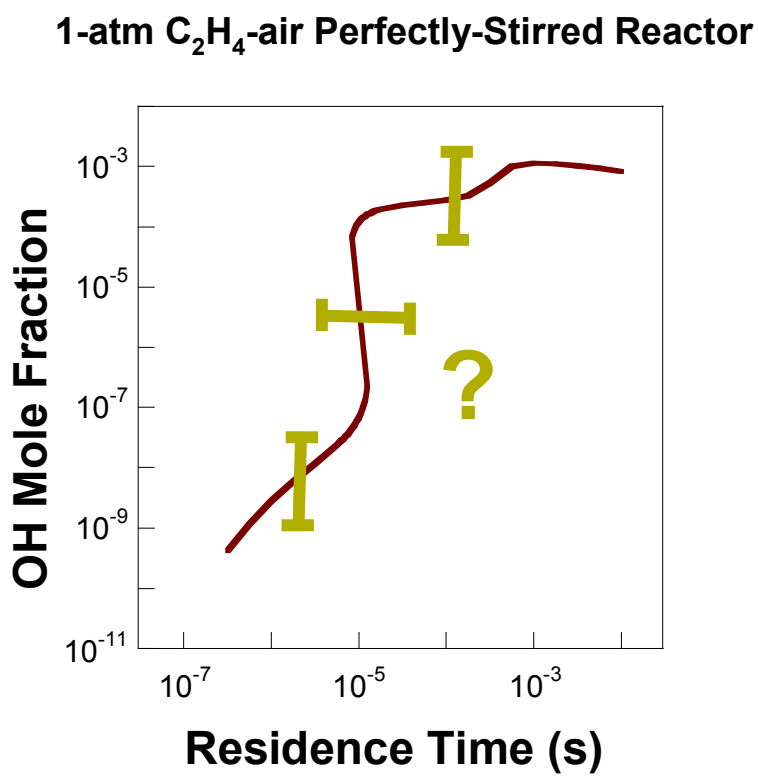
- ±5% (±4 cm/s) uncertainty in predicted flame speed due to R1 alone
- Key question: How to propagate uncertainties in rate constants in combustion simulations?

Baulch, *et al.* (2005)

Detailed Reaction Model Development

- Compile a trial reaction model from rate evaluation, *ab initio* methods, analogous reactions etc;
- Compare model predictions against laboratory flame experiments;
- Model reduction and application in more complex combustion problems;
- Determine the uncertainty in model predictions





Objectives

Develop a numerical approach for ***uncertainty quantification, propagation*** and ***minimization***

- **Forward propagation**

  σ **(trial kinetic model) → σ (computed combustion properties)**

- **Model optimization and reverse uncertainty propagation**

  σ **(experimental combustion data) → reduced σ (optimized model)**

- **Application in model reduction**

  Δ **(model reduction) ≤ σ (optimized model)**

Extend the **spectral expansion** method (Najm and coworkers) to uncertainty minimization

Methods

- **Stochastic Spectral Expansion:** express kinetic parameter x_i as a polynomial expansion of basis random variables

1st order coefficients

2nd order coefficients

$$x_i = x_i^{(0)} + \sum_{j=1}^{m} \alpha_{ij} \xi_j + \sum_{k=1}^{m} \sum_{j=k}^{m} \beta_{ijk} \xi_j \xi_k + \ldots$$

nominal value

basis random variable

Following N. Wiener (1938), D.B. Xiu, *et al.* (2002)

- **Solution Mapping**: use polynomial response surface to express the relation between a combustion response η and **x**

$$\eta_r(\mathbf{x}) \cong \eta_{r,0} + \sum_{i=1}^{N} a_{r,i} x_i + \sum_{i=1}^{N} \sum_{j \geq i}^{N} b_{r,ij} x_i x_j$$

Forward Uncertainty Propagation

$$\eta_r(\mathbf{x}) = \eta_{r,0} + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} \sum_{j \geq i}^{n} b_{ij} x_i x_j$$

Response surface from solution mapping

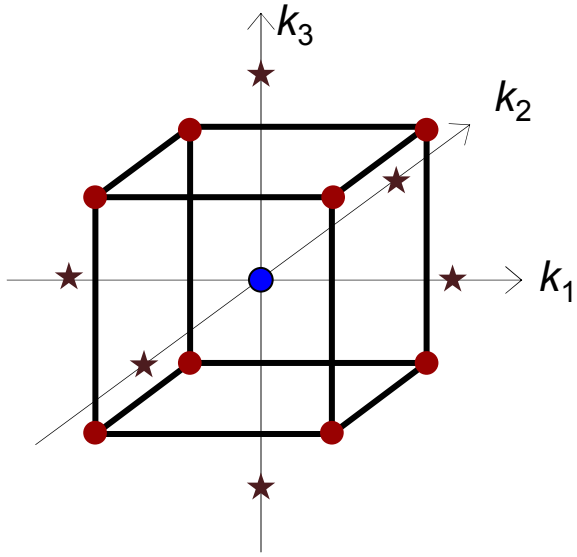
$$x_i = \tfrac{1}{2} \xi_i$$

Spectral representation of uncertainty in x's (mean = 0, σ = 0.5, each indep't of others)

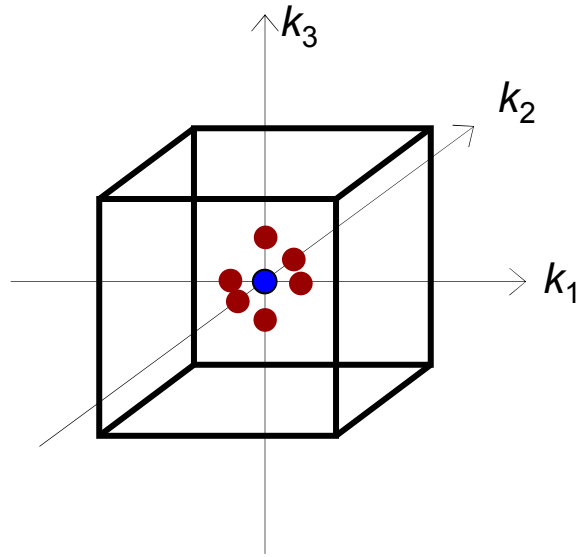
$$\boxed{\eta_r(\mathbf{x}, \boldsymbol{\xi}) = \eta_r\left(\mathbf{x}^{(0)}\right) + \sum_{i=1}^{M} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{M} \sum_{j=i}^{M} \hat{\beta}_{r,ij} \xi_i \xi_j}$$

Solution Mapping Method

- **Fit a response surface to the model**



Central-Composite Factorial Design

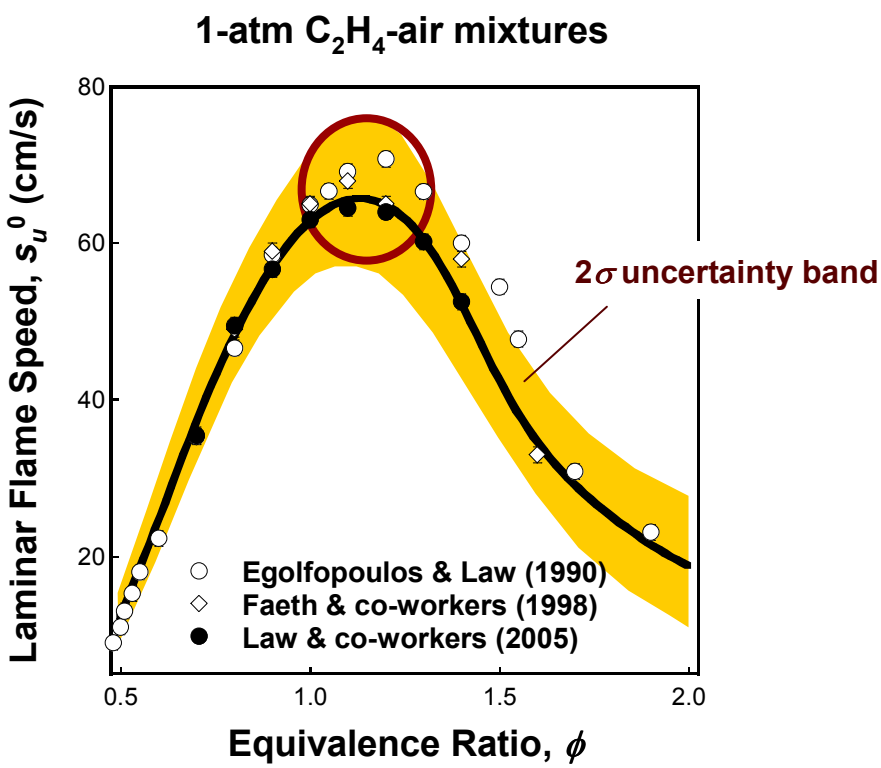


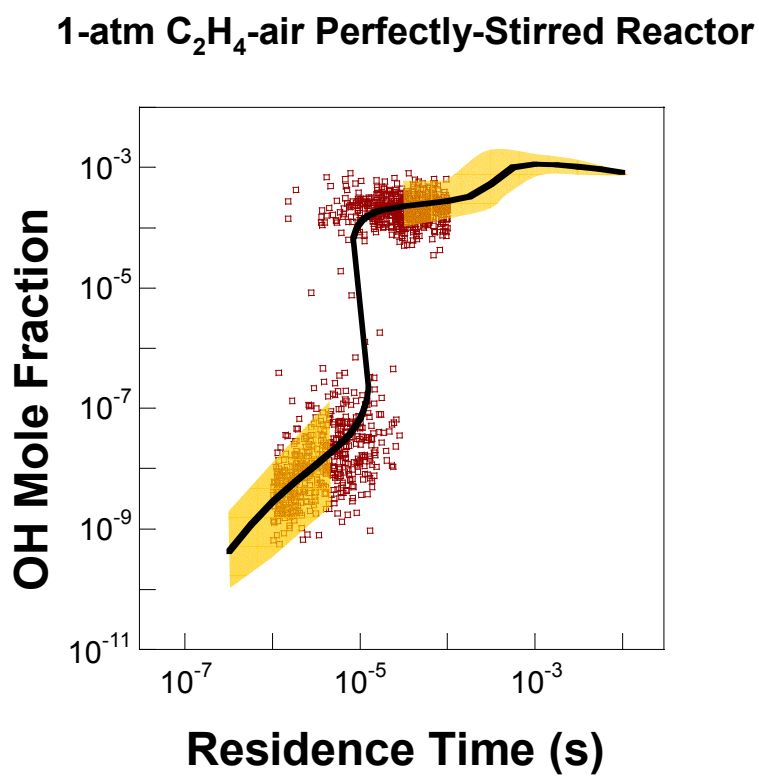
Sensitivity Analysis Based Design

G.E.P. Box, *et al.* (1978), Frenklach *et al*. (1992), S.G. Davis *et al.* (2004)

Forward Uncertainty Propagation (2)

- Compile a trial reaction model from rate evaluation, *ab initio* methods, analogous reactions etc;
- Compare model prediction against laboratory flame experiments;
- Model reduction and application in more complex combustion problems;
- **Determine the uncertainty in model predictions**





Reverse Uncertainty Propagation

Test Case: Ethylene Combustion

- Detailed reaction mechanism

  USC Mech II (111 species and 784 reactions)

Optimization Targets

	No.	P_0, P_5 (atm)	T_0, T_5 (K)	ϕ
Flame Speed	11	1-5	298	0.7-1.6
Ignition Delay	6	0.7-2.5	1200-2200	0.5-2
Flow Reactor	3	1	1000-1035	0.3-1.4
Flat Flame	2	0.026	432	1.9

Optimization Method

- **Solution mapping/model optimization**

$$\eta_r(\mathbf{x}) = \sum_{i=1}^{n}\sum_{j\geq i}^{n} a_{ij}x_i x_j + \sum_{i=1}^{n} b_i x_i + \eta_{r,0}$$

Response surface from solution mapping

Experimental target

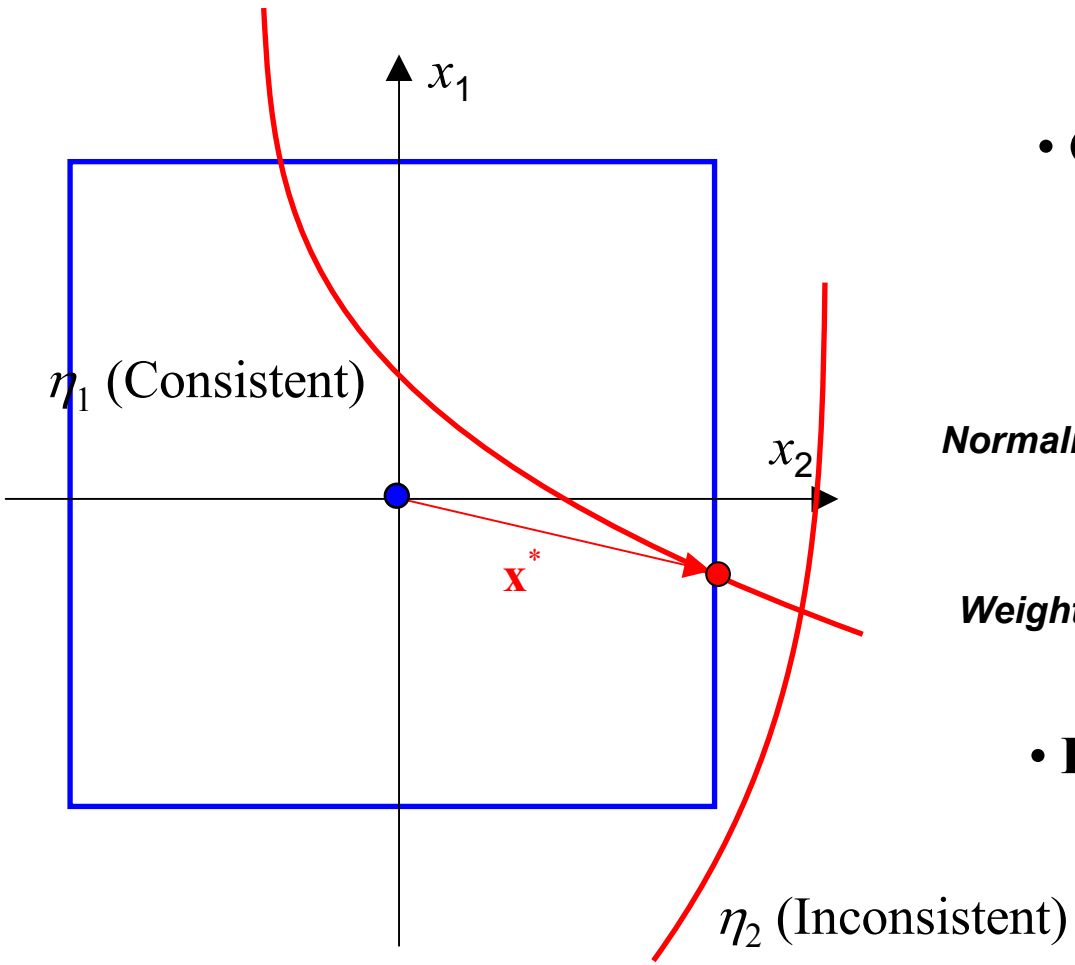
$$\Phi(\mathbf{x}^*) = \min_{\mathbf{x}} \sum_{r=1}^{n} \frac{1}{\left(\sigma_r^{\text{obs}}\right)^2}\left[\eta_r^{\text{obs}} - \eta_r(\mathbf{x})\right]^2$$

Get model to reproduce observations as closely as possible

Model response

Frenklach, Wang & Rabinowitz (1992)

Data Set Consistency



- **Consistency Measure:**

Objective Function $$F_r = \frac{\eta_r^{\text{obs}} - \eta_r\left(\mathbf{x}^*\right)}{2\sigma_r}$$

Normalized scalar product $$S_r = \frac{\nabla \eta_r\left(\mathbf{x}^*\right) \cdot \mathbf{x}^*}{\left\|\nabla \eta_r\left(\mathbf{x}^*\right)\right\| \left\|\mathbf{x}^*\right\|}$$

Weighted scalar product $$W_r = S_r F_r$$

- **Inconsistent targets removed in order of W_r**

Reverse Uncertainty Propagation (2)

Model optimization & uncertainty minimization

$$\eta_r^{\text{obs}}(\boldsymbol{\xi}) = \eta_{r,0}^{\text{obs}} + \sigma_r^{\text{obs}} \xi_r$$

Each observable under a given condition is independent of other conditions

$$\eta_r(\mathbf{x}, \boldsymbol{\xi}) = \eta_r\left(\mathbf{x}^{(0)}\right) + \sum_{i=1}^{M} \hat{\alpha}_{r,i} \xi_i + \sum_{i=1}^{M} \sum_{j=i}^{M} \hat{\beta}_{r,ij} \xi_i \xi_j$$

Uncertainty expression from SM/SSE

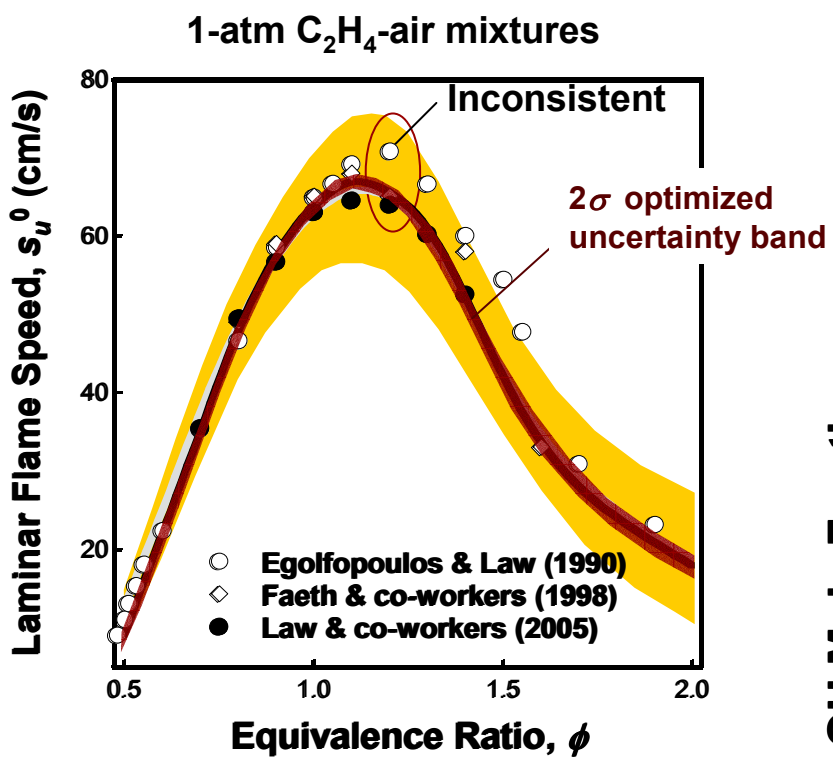
Original optimization problem

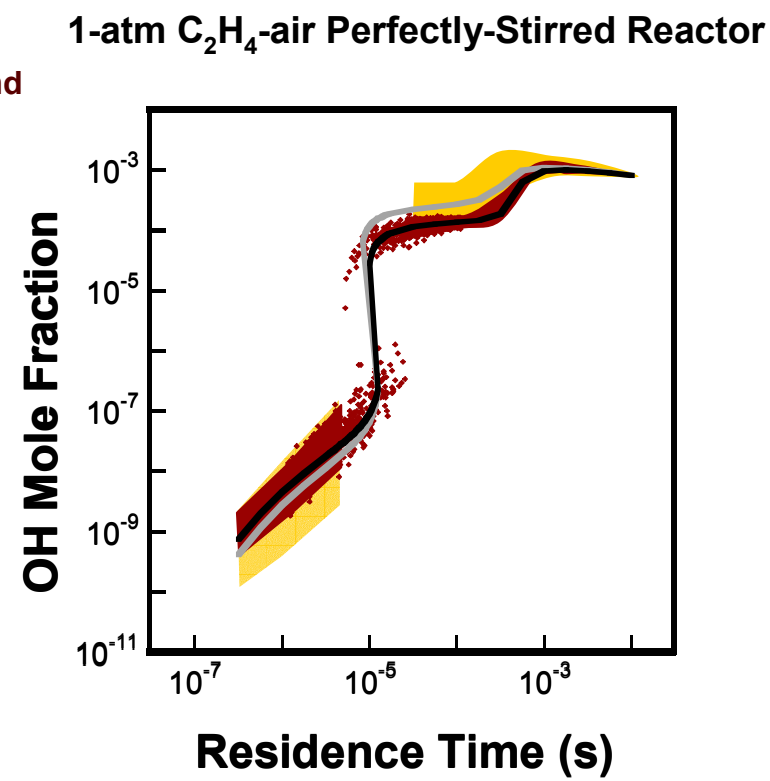
$$\Phi\left(\mathbf{x}^{(0)*}, \boldsymbol{\alpha}^*, \boldsymbol{\beta}^*\right) = \min_{\left\{\mathbf{x}^{(0)}, \boldsymbol{\alpha}, \boldsymbol{\beta}\right\}} \sum_{r=1}^{M} \frac{1}{\left(\sigma_r^{\text{obs}}\right)^2} \left\{ \left[\eta_{r,0}^{\text{obs}} - \eta_r(\mathbf{x}_0)\right]^2 + \sum_{i=1}^{M} \left[\sigma_r^{\text{obs}} \delta_{ir} - \hat{\alpha}_{r,i}\right]^2 + \sum_{i=1}^{M} \sum_{j=i}^{M} \hat{\beta}_{r,ij} + \ldots \right\}$$

Optimize model uncertainty against observed uncertainty

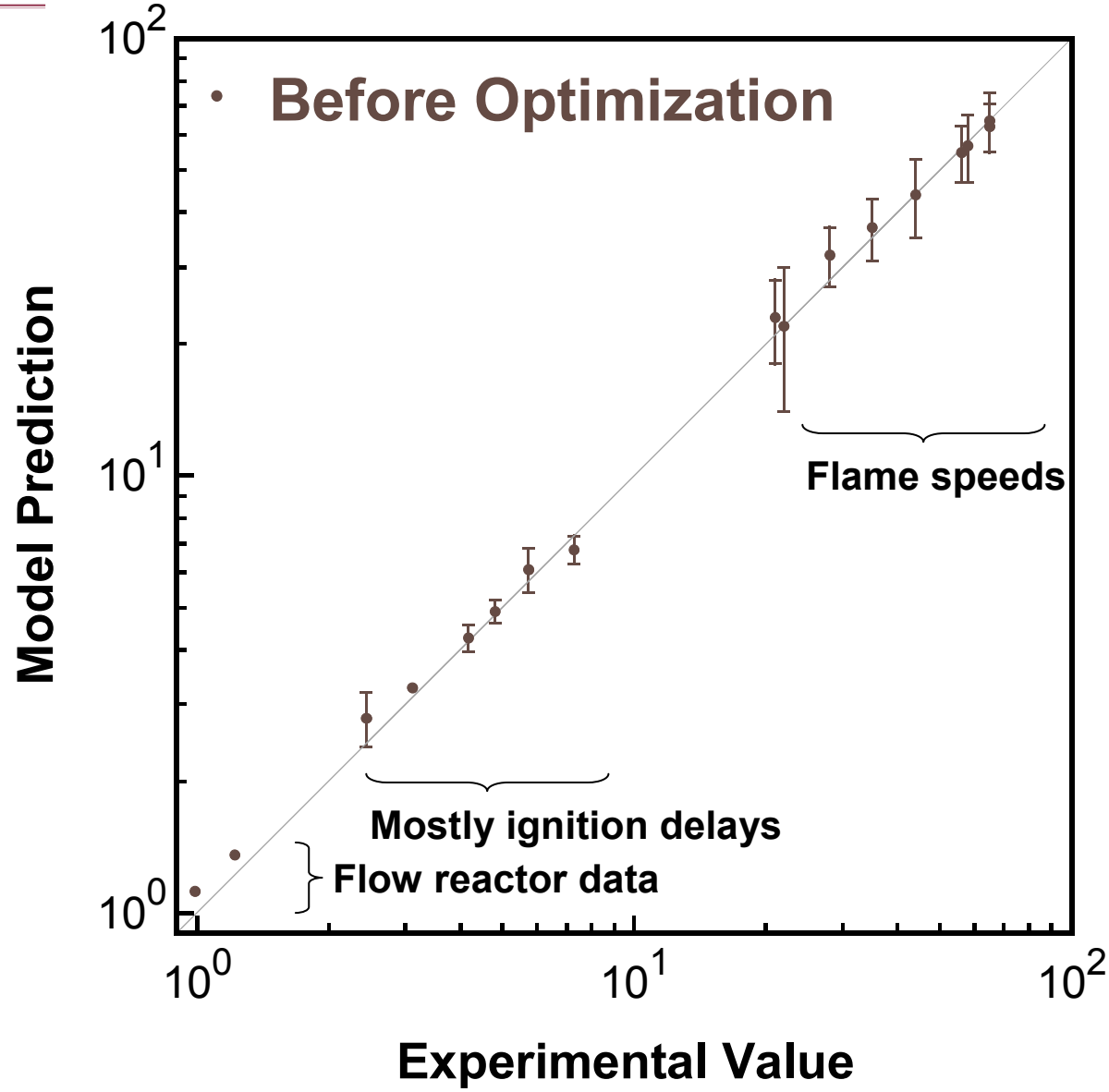
Reverse Uncertainty Propagation (3)

- Compile a trial reaction model from rate evaluation, *ab initio* methods, analogous reactions etc;
- Compare model prediction against laboratory flame experiments;
- Model reduction and application in more complex combustion problems;
- Determine the uncertainty in model predictions
- **Model optimization and uncertainty minimization**





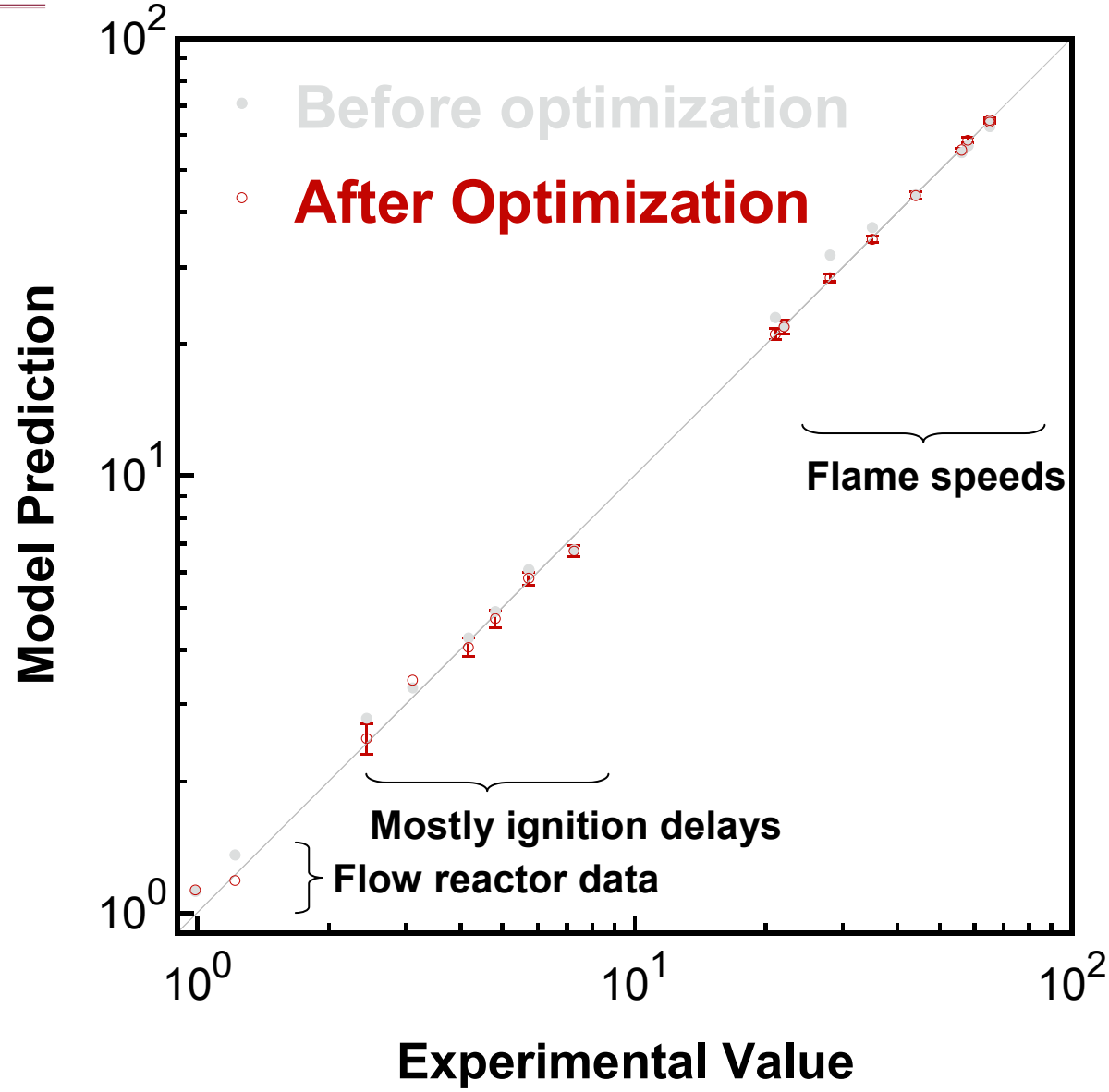
Optimization Results (1)



ΔS_u^o ±8 cm/s

$\Delta \tau_{ign}$ ±50%

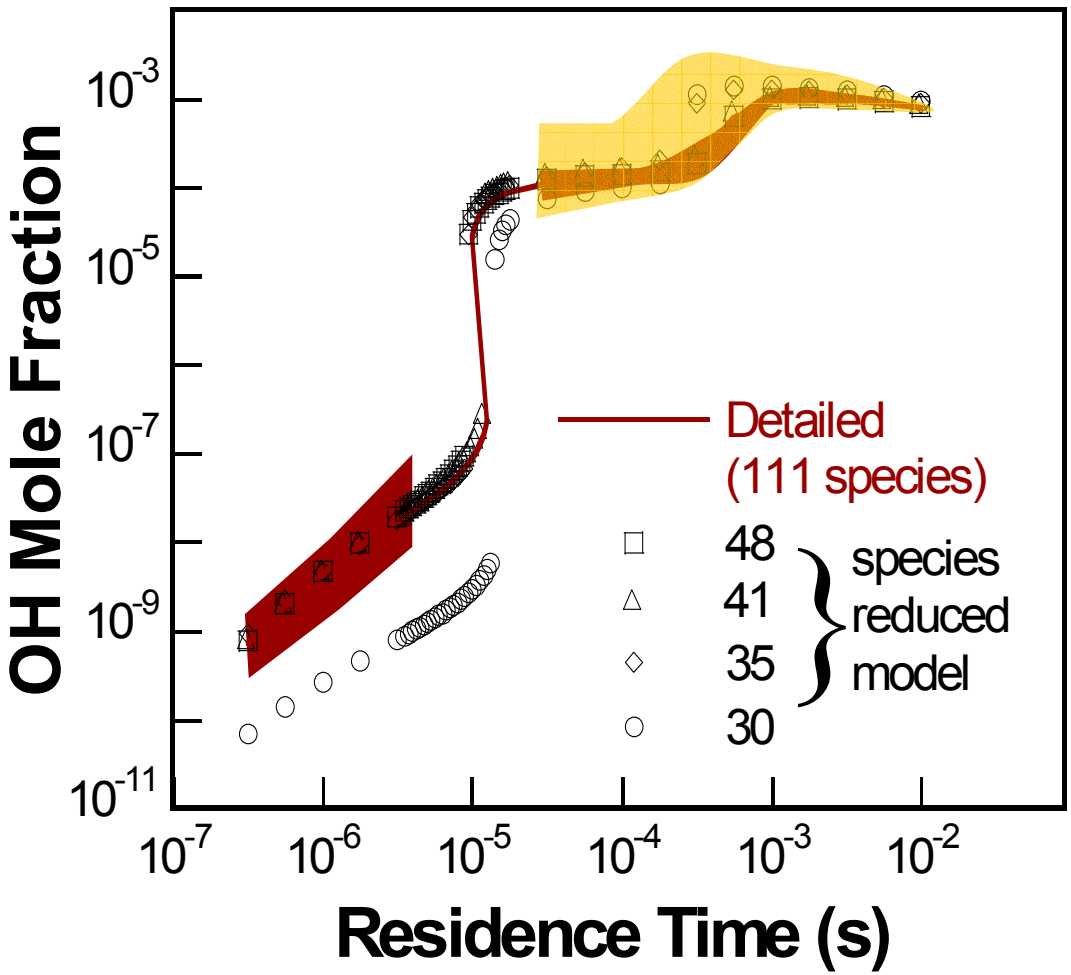
Optimization Results (2)



ΔS_u^o ±1 cm/s

$\Delta \tau_{ign}$ ±20%

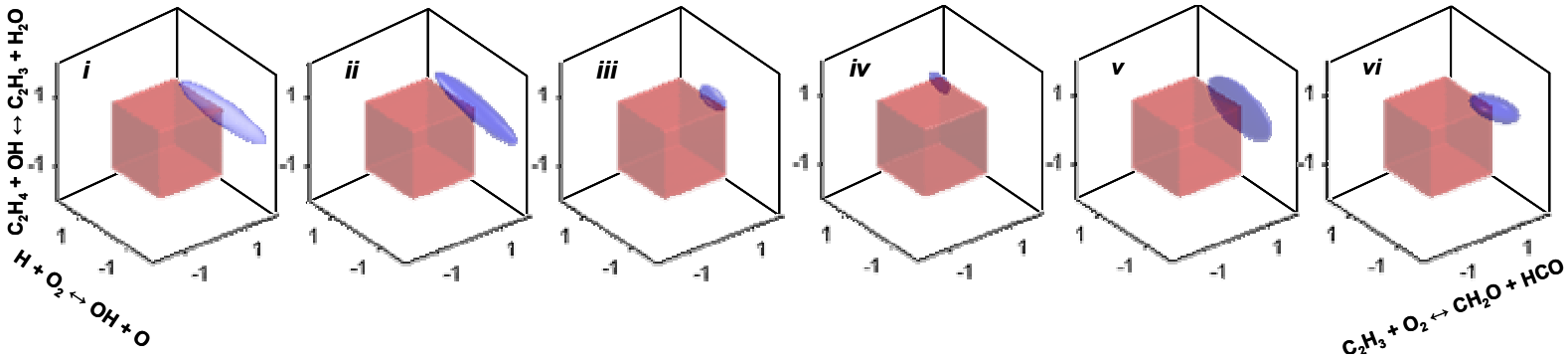
Implication on Model Reduction



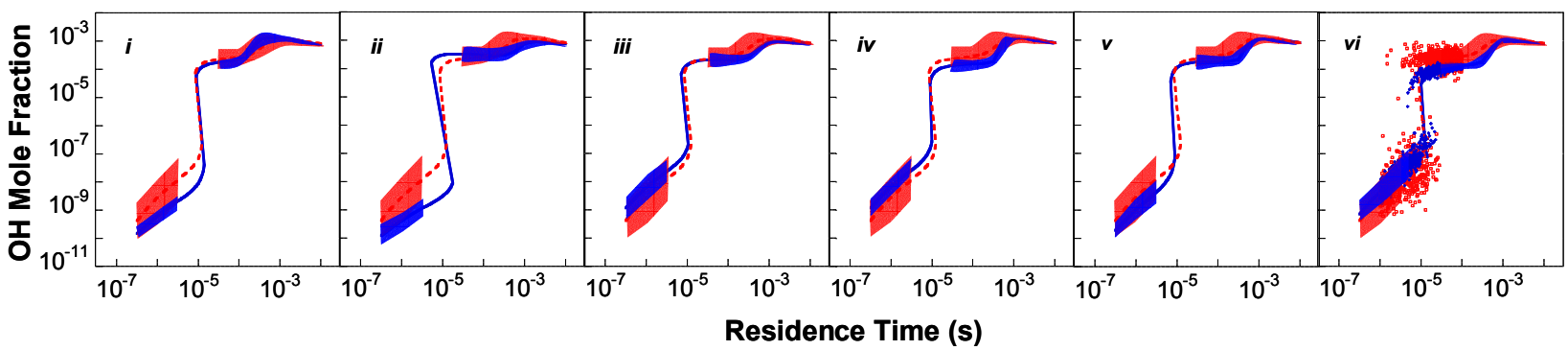
Model reduction by the LOI method (Løvås, *et al.* 2002)

Model Evolution

Are we converging on a predictive model?



≤ 1990 | ≤ 1999a | ≤ 1999b | ≤ 1999 (all) | ≤ 2000 (all) | Today



Uncertainty - Concluding Remarks

- **Spectral expansion** method is combined with **solution mapping** to quantify and propagate kinetic uncertainty
- Method of combustion **data consistency** is proposed
- The methods were applied to a model of ethylene combustion
- New criterion for model reduction: reduced model need only be compared to detailed model uncertainty