Combustion Chemistry in the Twenty-First Century: Developing a Theory-Informed Chemical Kinetic Model for the Small-Hydrocarbon Fuels

James A. Miller

Argonne National Laboratory

Collaborators/Co-Authors/Partners

- Stephen Klippenstein
- Raghu Sivaramikrishnan
- Michael Burke (Columbia)
- Franklin Goldsmith (Brown)
- Yuri Georgievski
- Larry Harding
- Branko Ruscic

- Ahren Jasper
- Judit Zádor
- Nils Hansen

- Peter Glarborg

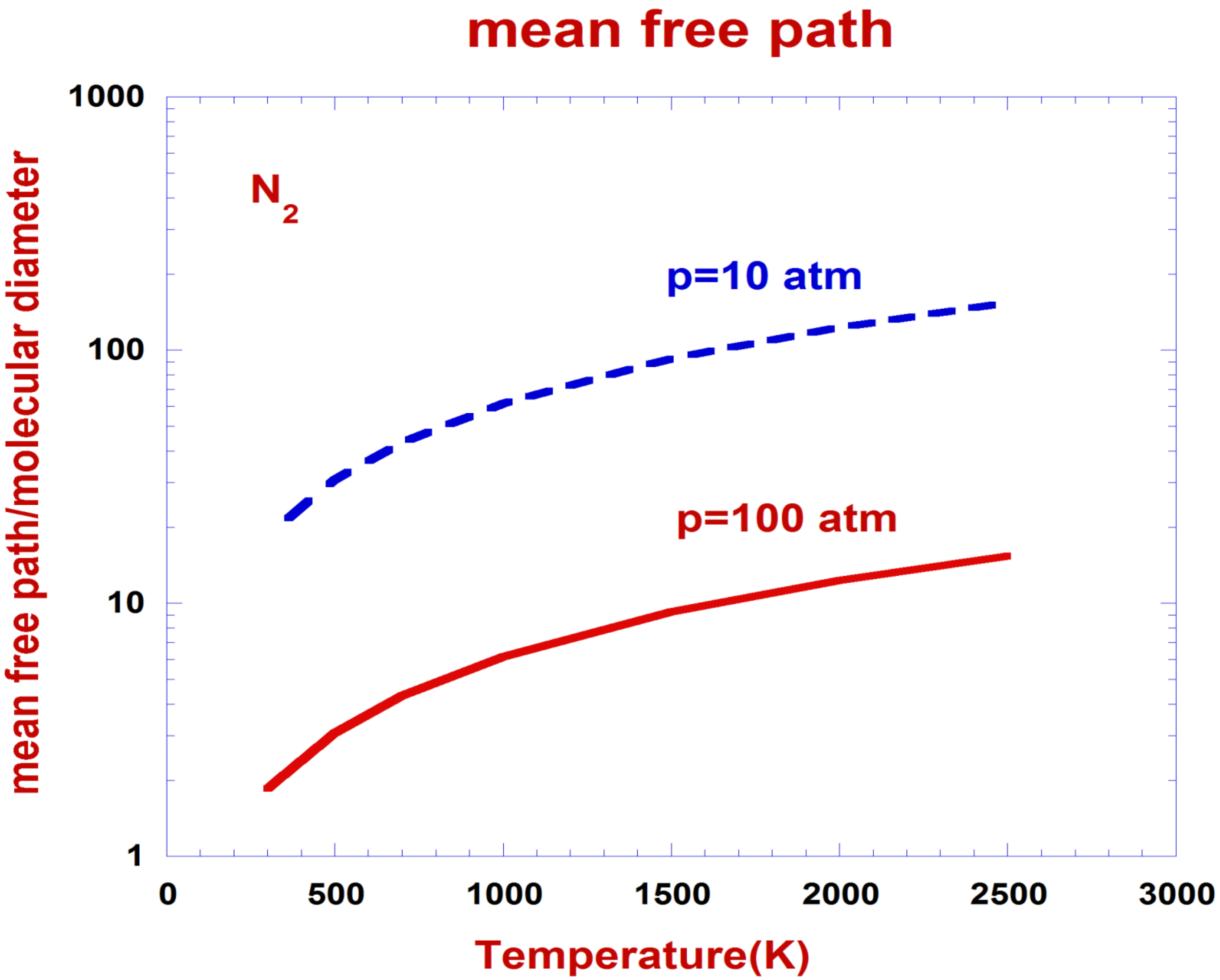
Support

- **Argonne-Sandia High-Pressure Combustion Consortium – DOE Office of Basic Energy Sciences**

Distinguishing Characteristics of Present Model

- Focus on C_0-C_3 chemistry (plus methanol and ethanol)– molecules large enough to exhibit low-temperature chemistry, small enough to be attacked with high-level electronic-structure methods
- Relies heavily on theory (thermochemistry, transport, chemical kinetics)
- Focus on extension to high pressure
- No fitting, no “optimization”, no adjustable parameters

What does “high pressure” mean?



Thermochemistry

- **Active Thermochemical Tables**
- **Very High-Level Electronic Structure Theory:**

  C-H-O-N species with 34 or fewer electrons – 4 (or 5) heavy atoms

High Accuracy *Ab Initio* Thermochemistry

Central Elements

- **CCSD(T)/TZ rovibrational analysis**
- **CCSD(T)/CBS(AQZ,A5Z)**
- **CCSDT(Q)/DZ – CCSD(T)/DZ**

Minor Corrections

- **Core-Valence CCSD(T,full)/CBS(pcVTZ,pcVQZ)**
- **Anharmonic Vibration Corrections B3LYP or MP2**
- **Relativistic CI(aug-cc-pcvtz)**
- **Diagonal Born-Oppenheimer HF/TZ**

2 σ Accuracy ~ 0.2 kcal/mol

Replace with CASPT2 and/or CI+QC as necessary

Transport Properties

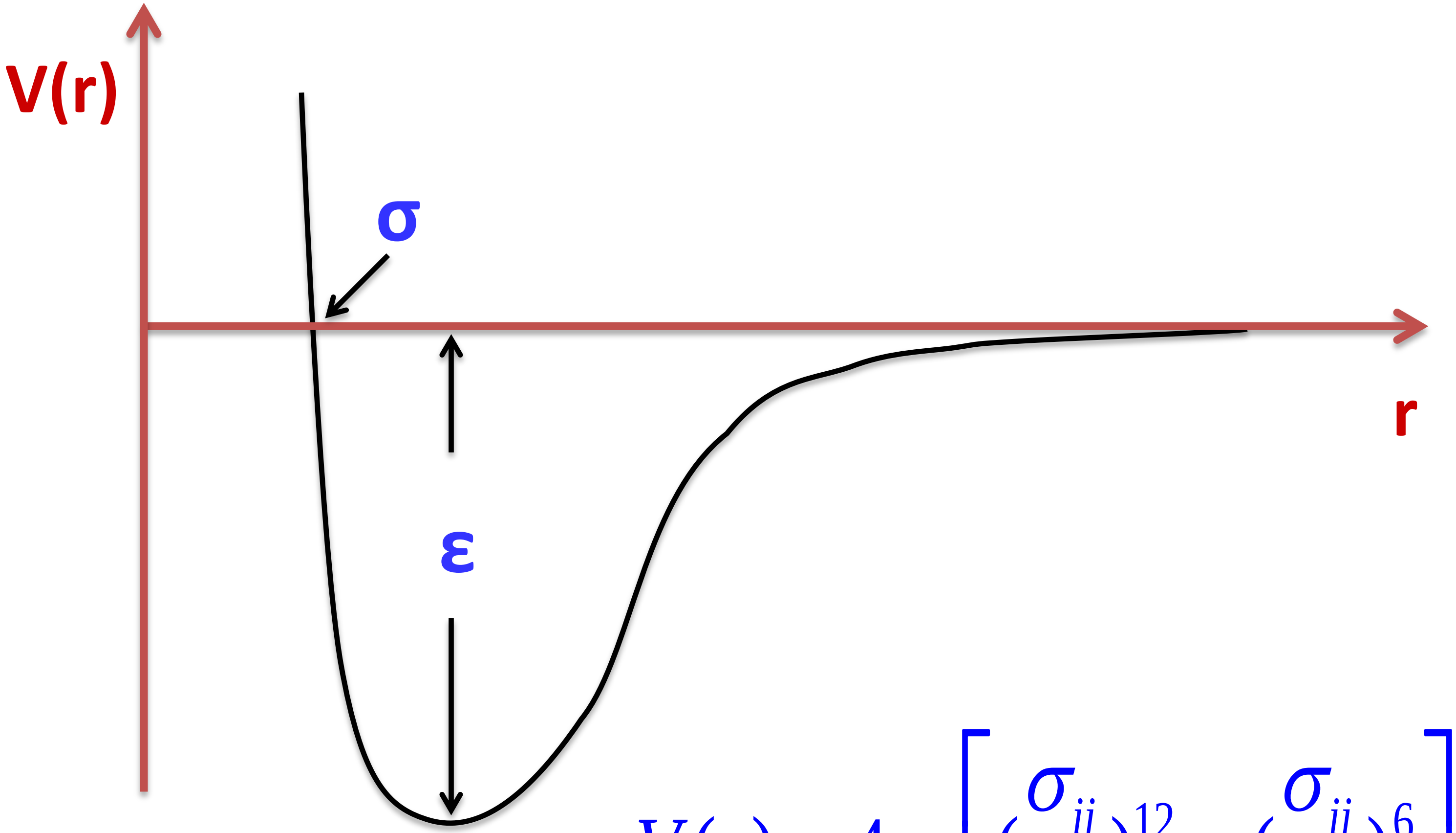
2 Objectives

1. Provide accurate Lennard-Jones parameters for use in flame calculations
2. Test accuracy of isotropic/Lennard-Jones potential

Methods

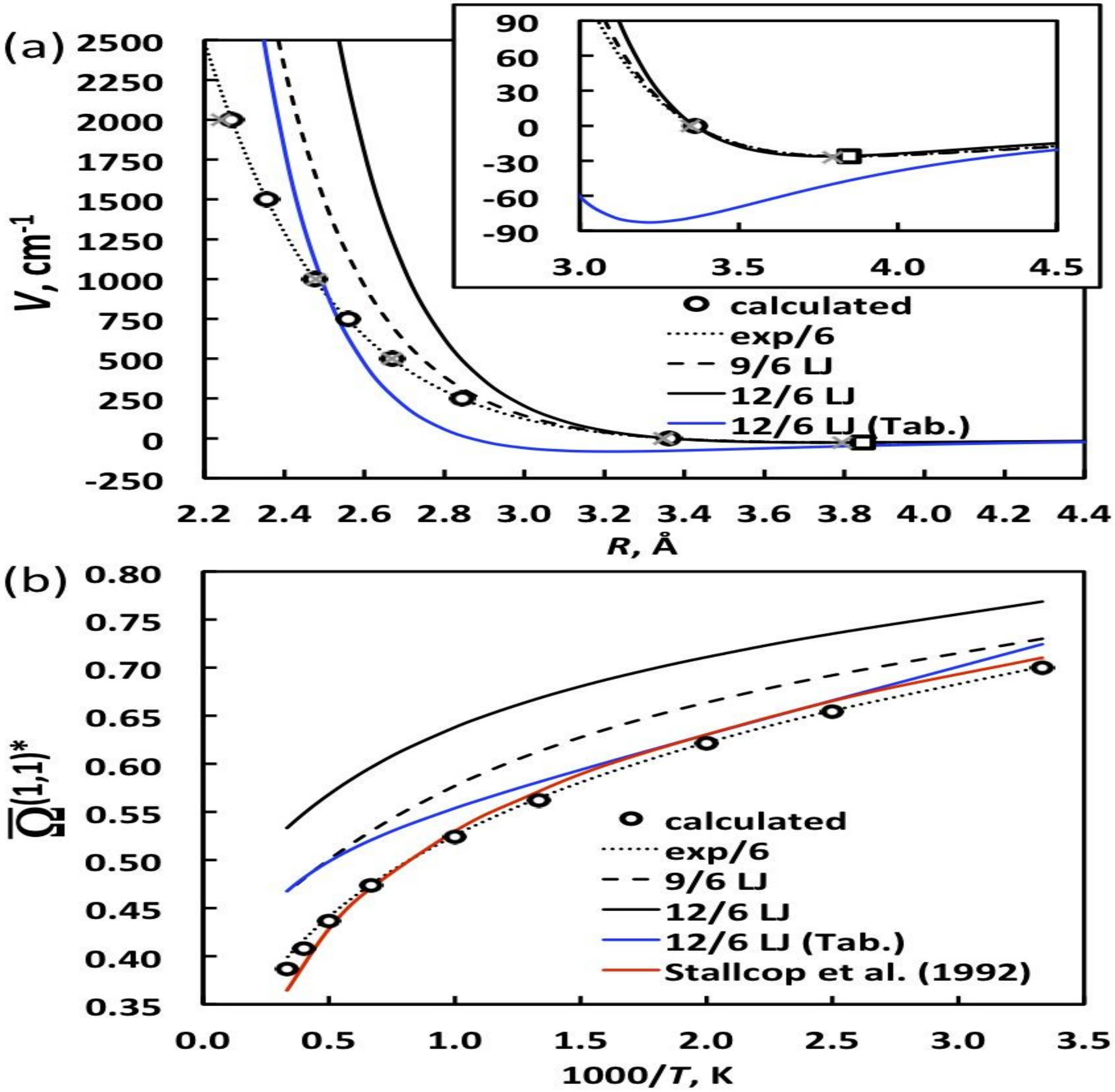
- Calculate σ and ε for N_2- X from "isotropically averaged potential" using MP2/aug'dz method – use combining rules to get self parameters
- Calculate collision integral (diffusion) "exactly" from classical trajectories using fitted potentials
- Calculate dipole moments and polarizabilities from high-level electronic structure theory

Lennard-Jones Potential

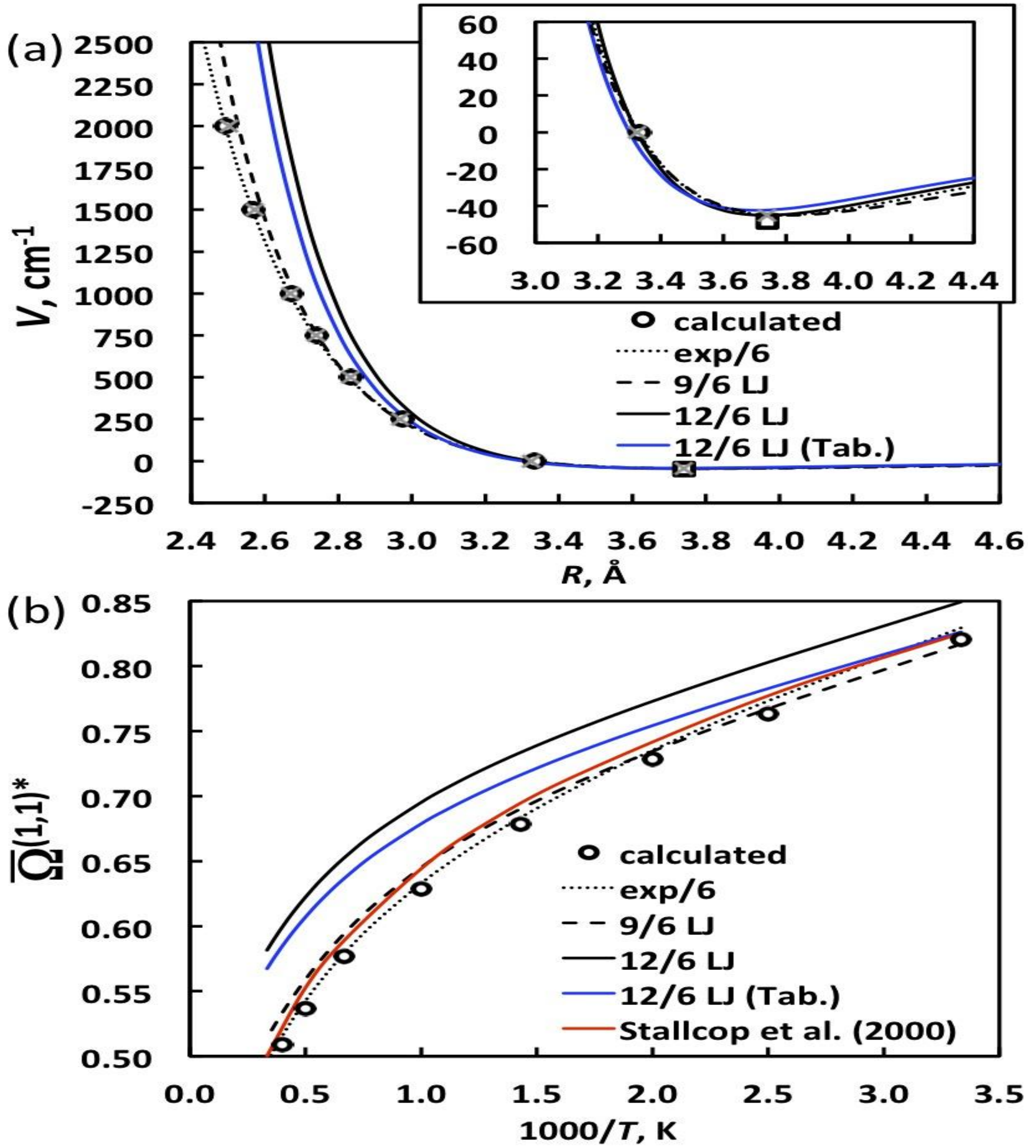


$$V(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

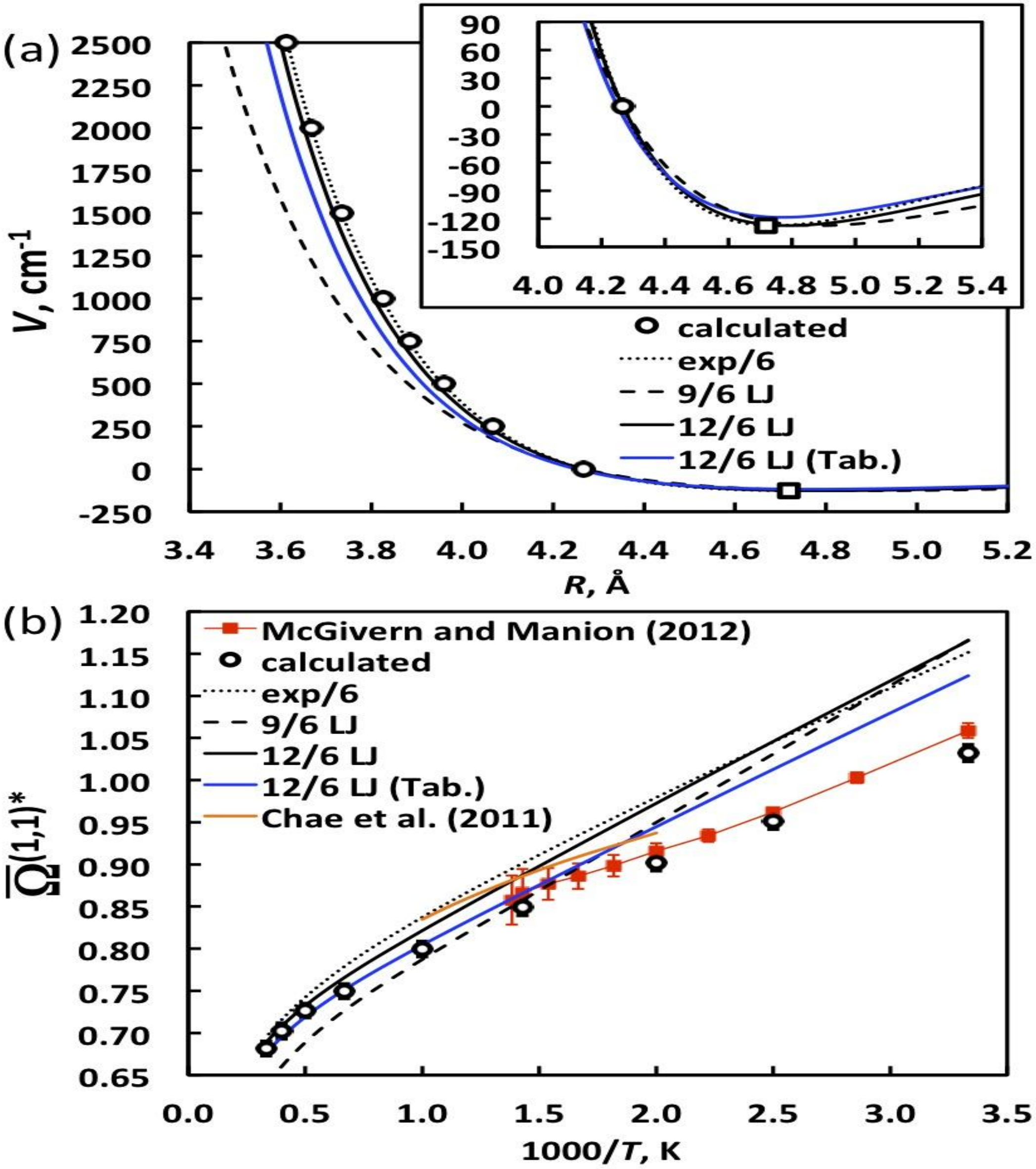
$H - N_2$ interaction



H_2 –N_2 interaction



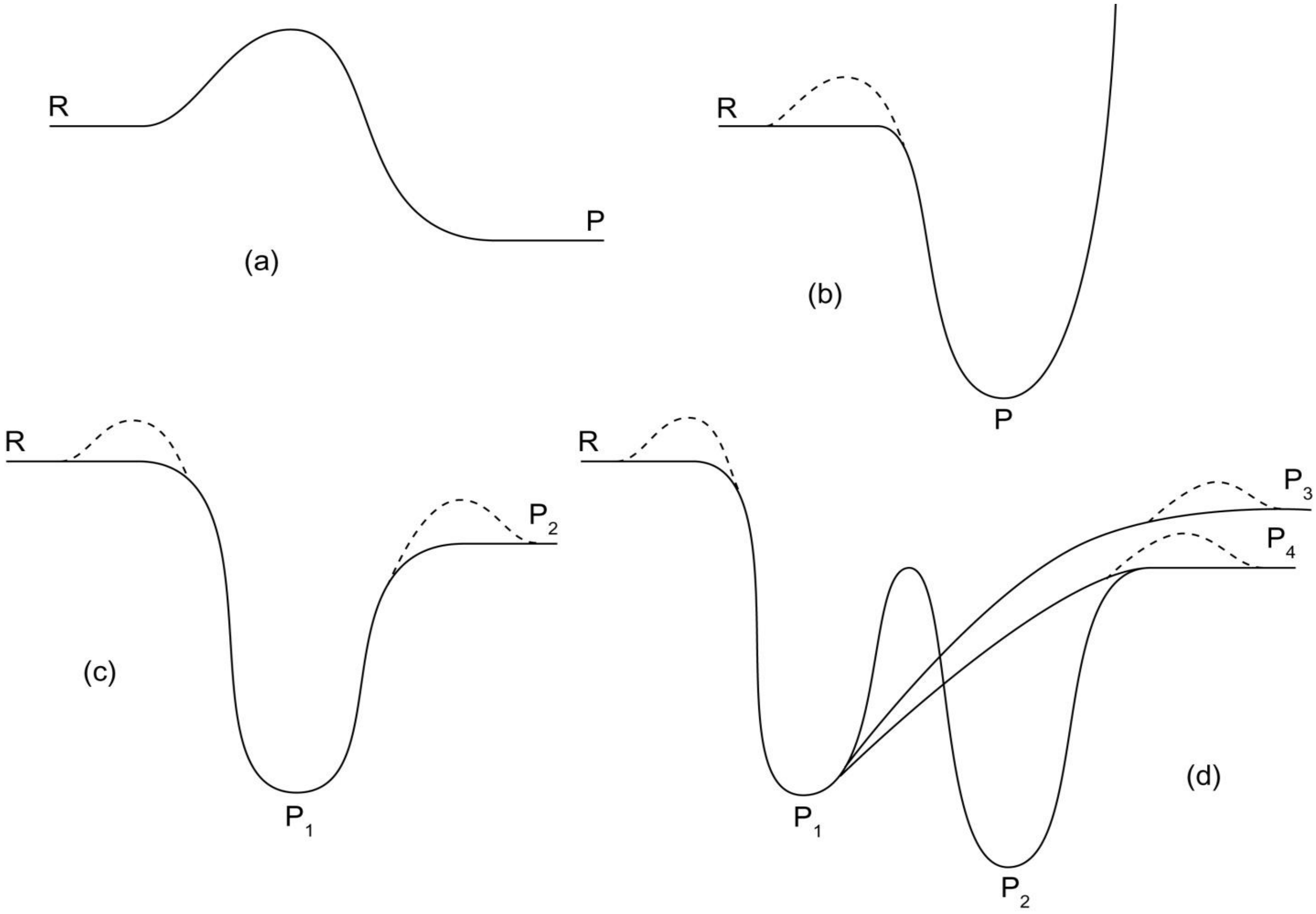
$C_3H_8 - N_2$ interaction



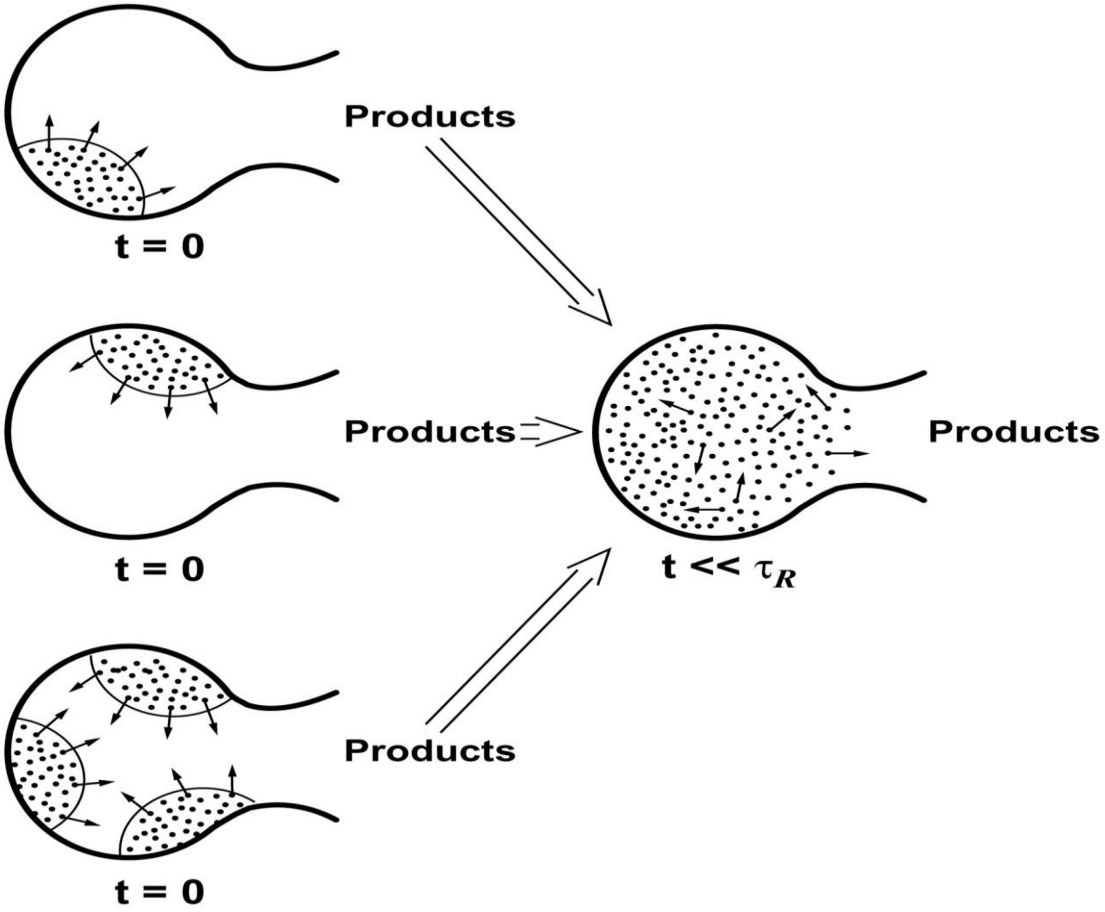
Chemical Kinetics

- RRKM/non-RRKM behavior
- Dissociation of weakly-bound free radicals
- Multiple-well, multiple-product-channel problems

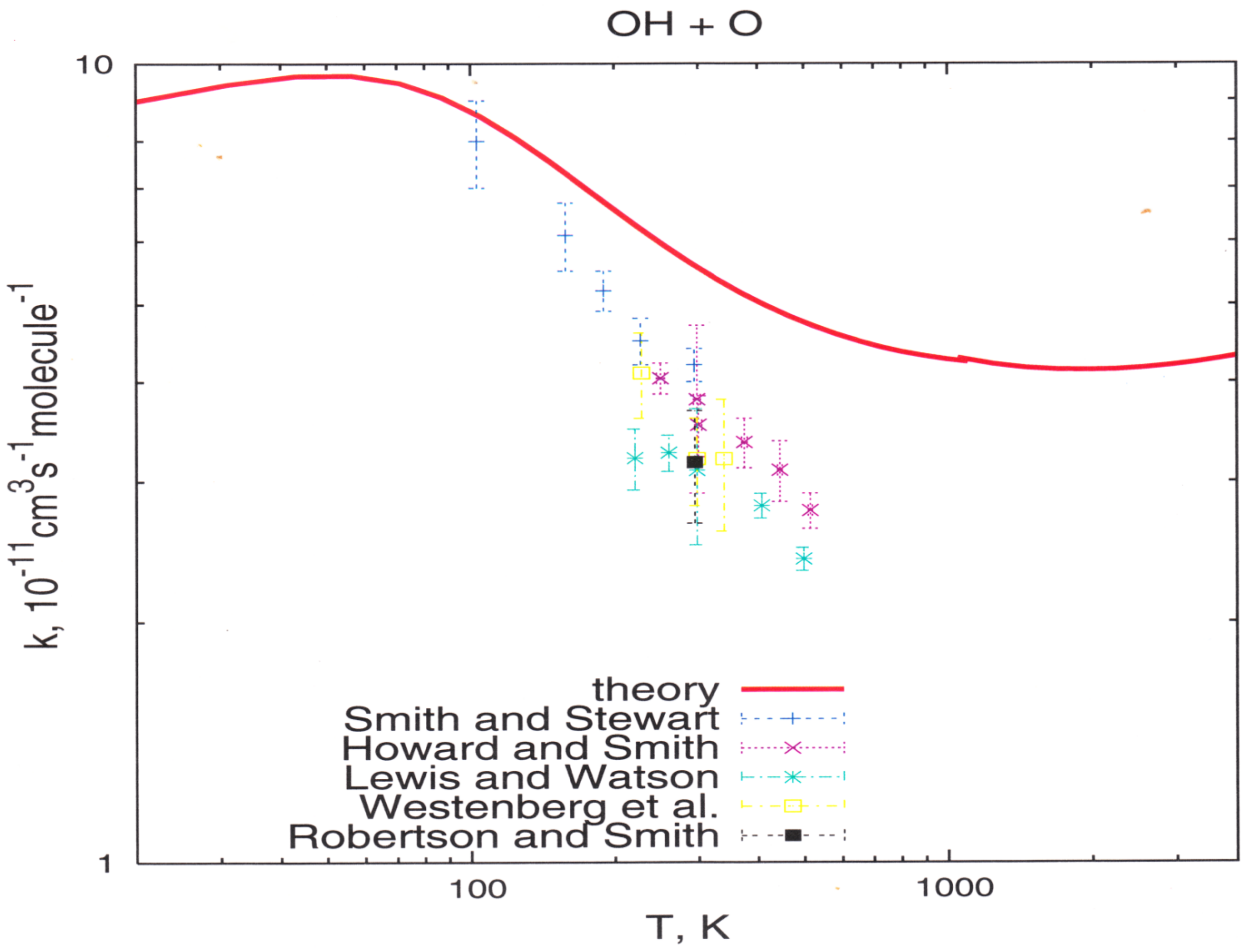
Types of Chemical Reactions

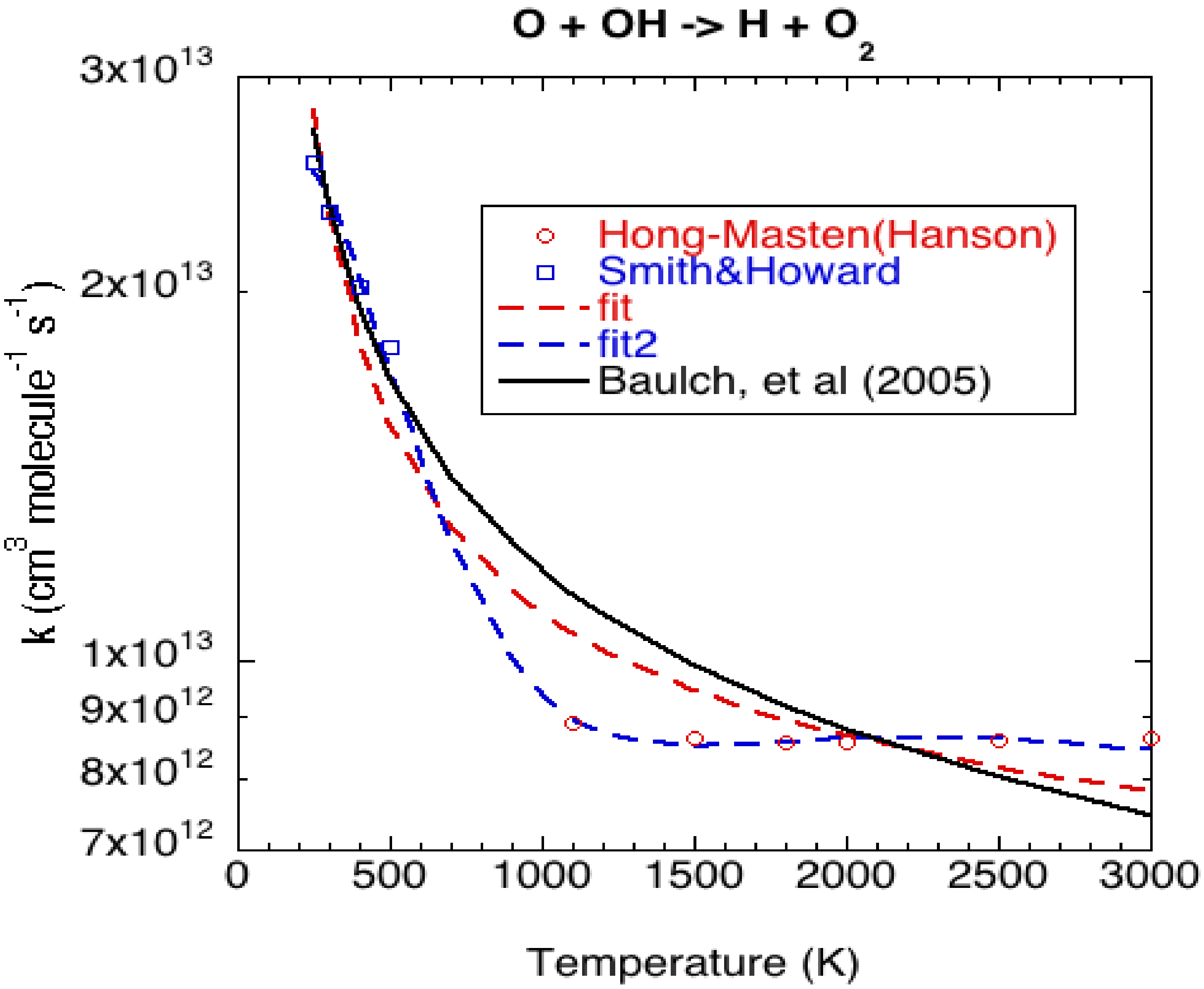


RRKM Intramolecular Dynamics



$H+O_2 \rightleftarrows OH+O$

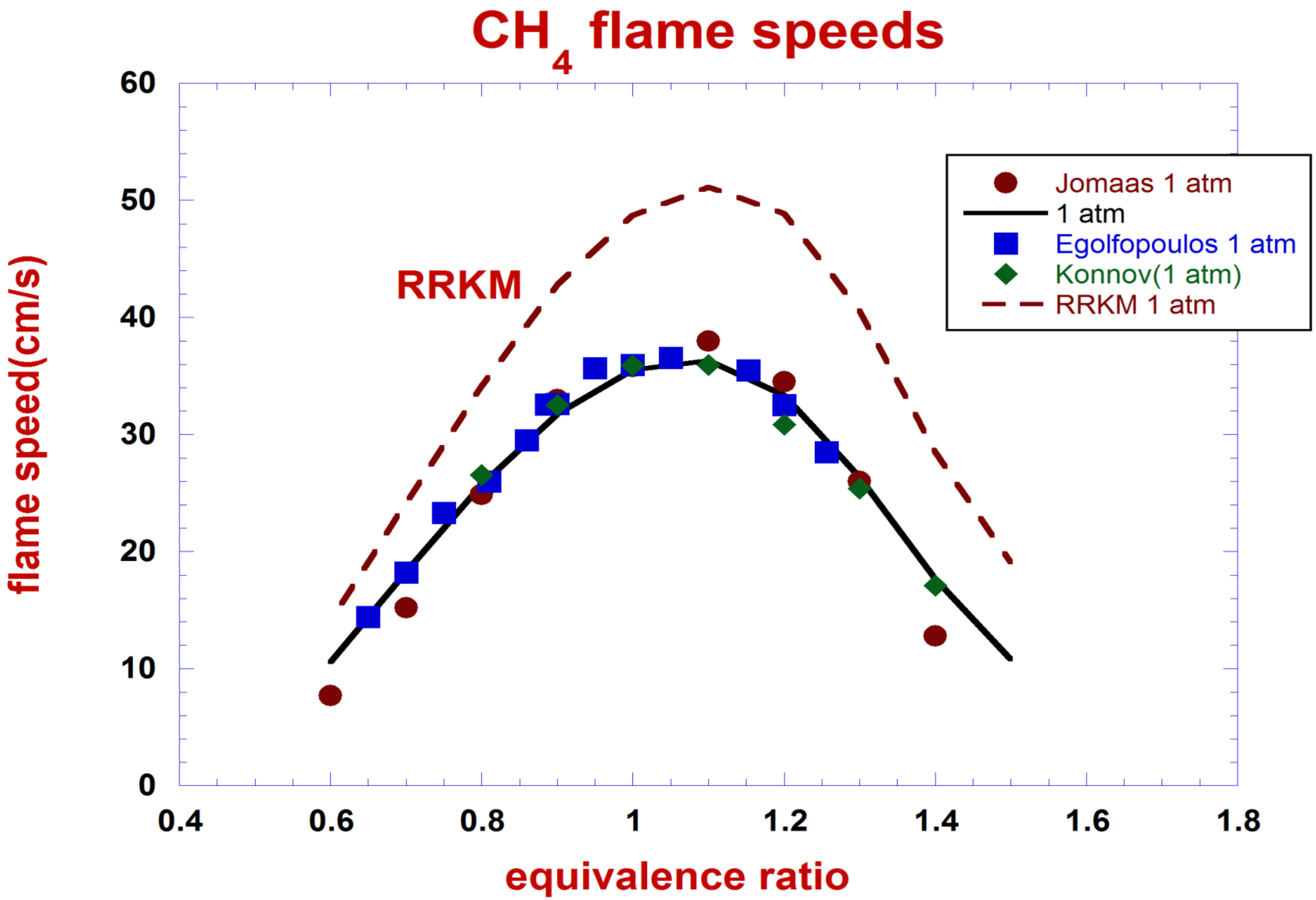




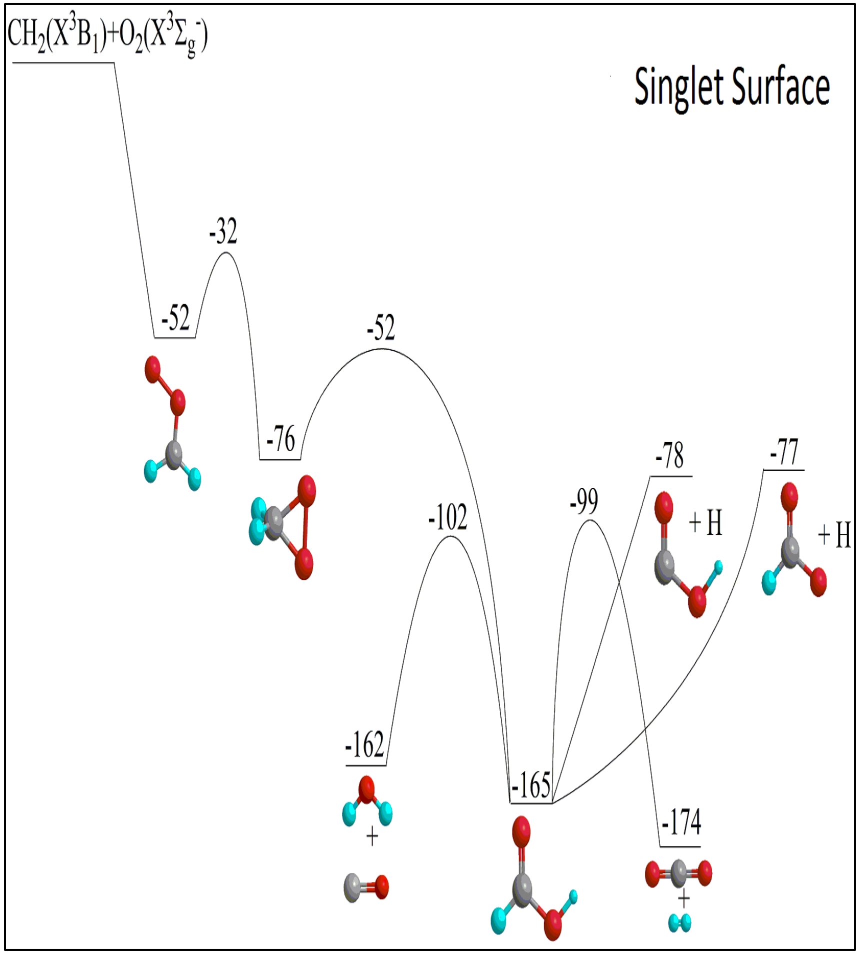
O + OH -> H + O_2

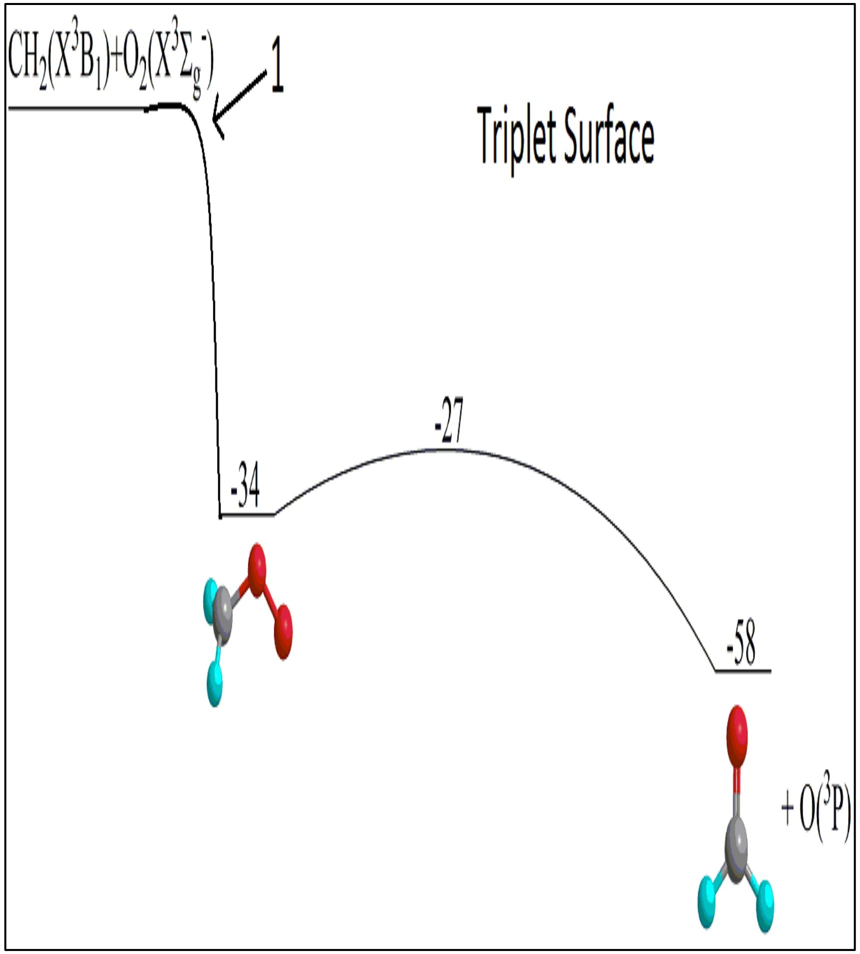
3x10^13
2x10^13
1x10^13
9x10^12
8x10^12
7x10^12
k (cm^3 molecule^-1 s^-1)
0
500
1000
1500
2000
2500
3000
Temperature (K)
Hong-Masten(Hanson)
Smith&Howard
fit
fit2
Baulch, et al (2005)

Effect of non-RRKM Behavior in $H+O_2 \rightleftarrows OH+O$



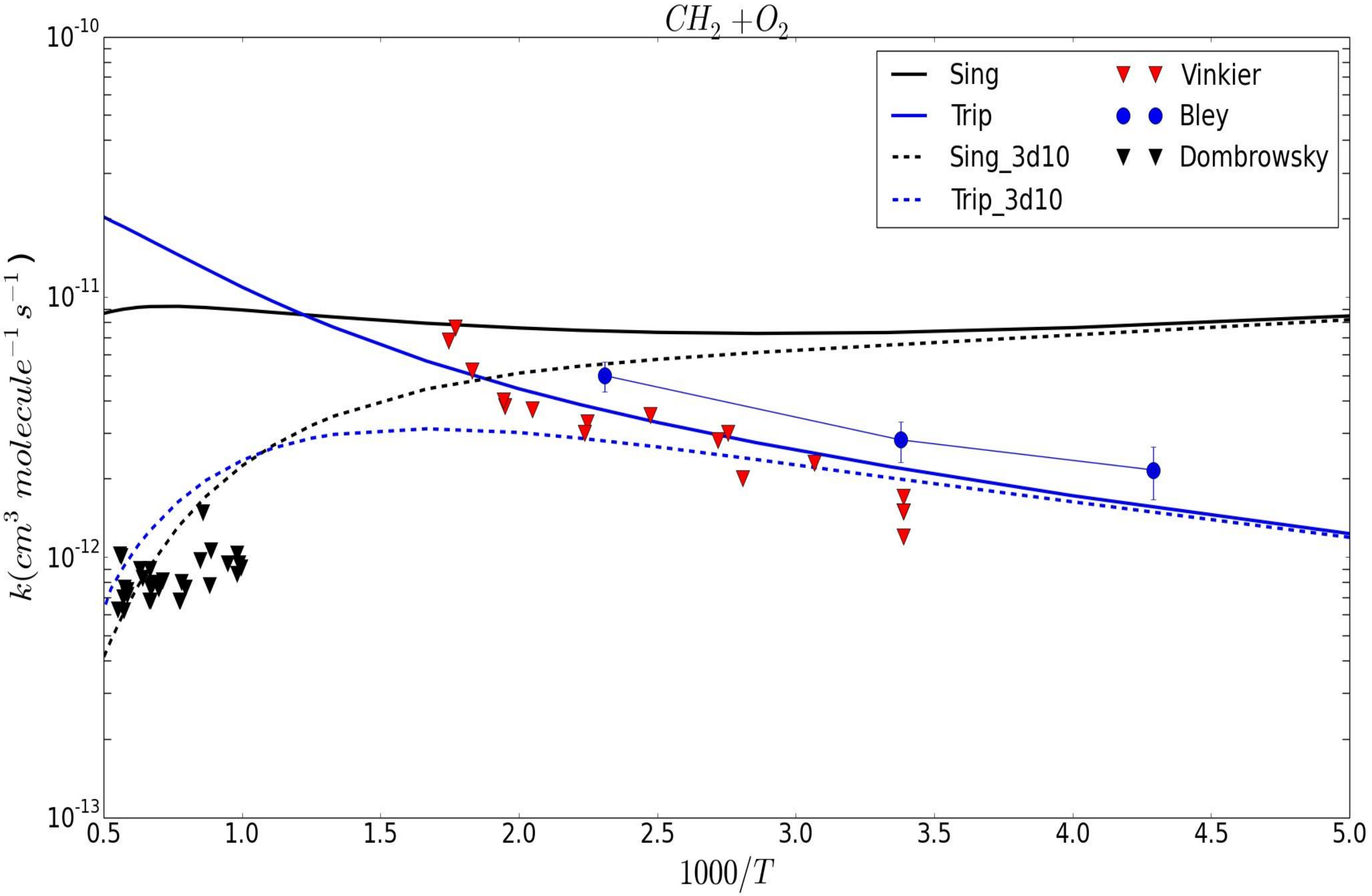
$^{3}CH_2+O_2 \rightarrow$products





Courtesy of Alex Landera

$^3CH_2$+O_2 Rate Constants

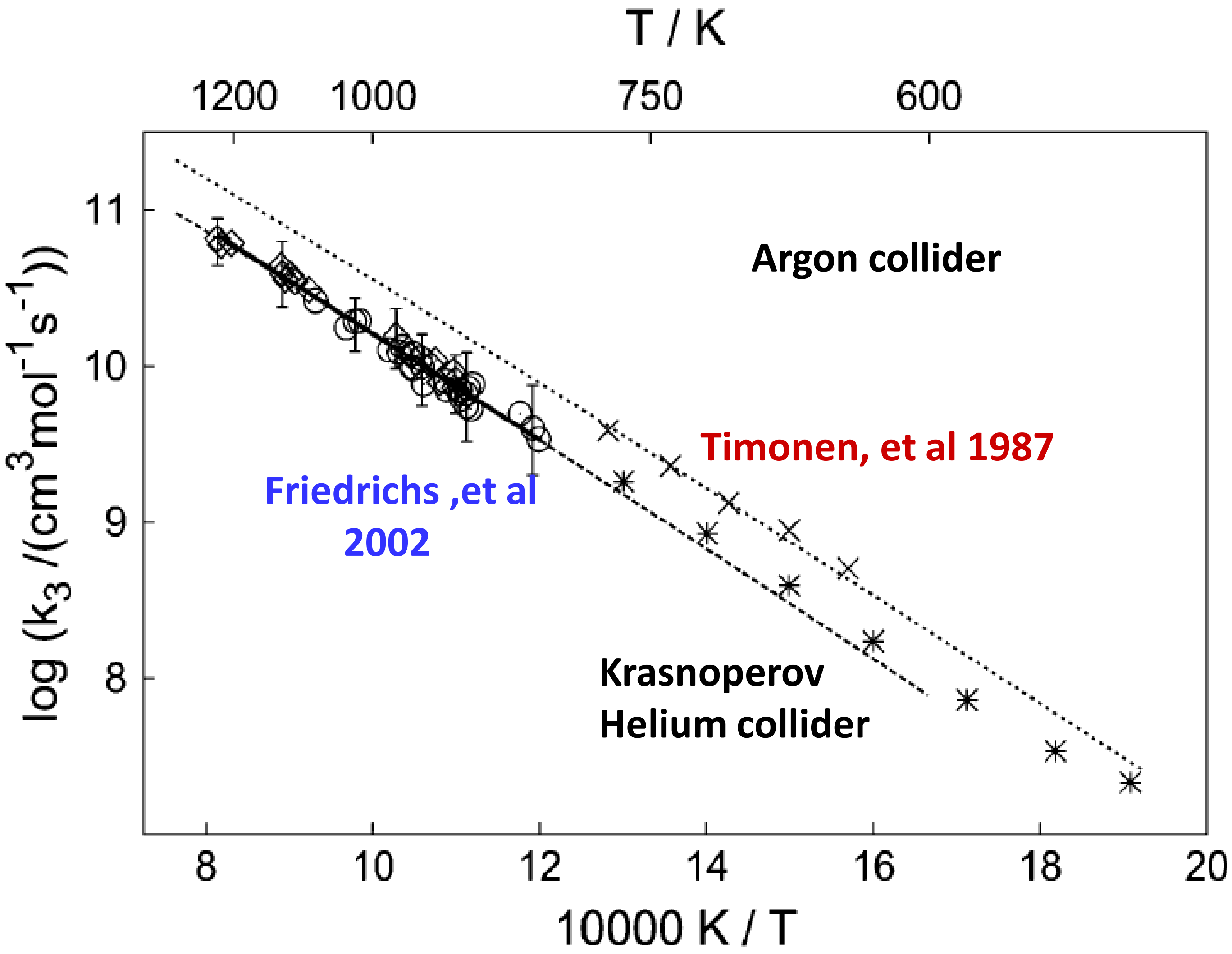


Courtesy of Alex Landera

Weakly-bound free radicals

- Dissociate primarily to form stable molecule and another free radical
- Low threshold energies for dissociation (**weak bonds**) with "intrinsic" potential energy barriers
- Examples: vinyl, ethyl, n- and i-propyl (all alkyl radicals), **allyl**, **formyl**, …
- *Not* weakly bound- methyl, propargyl, …

The Dissociation of Formyl Radical



Argon collider

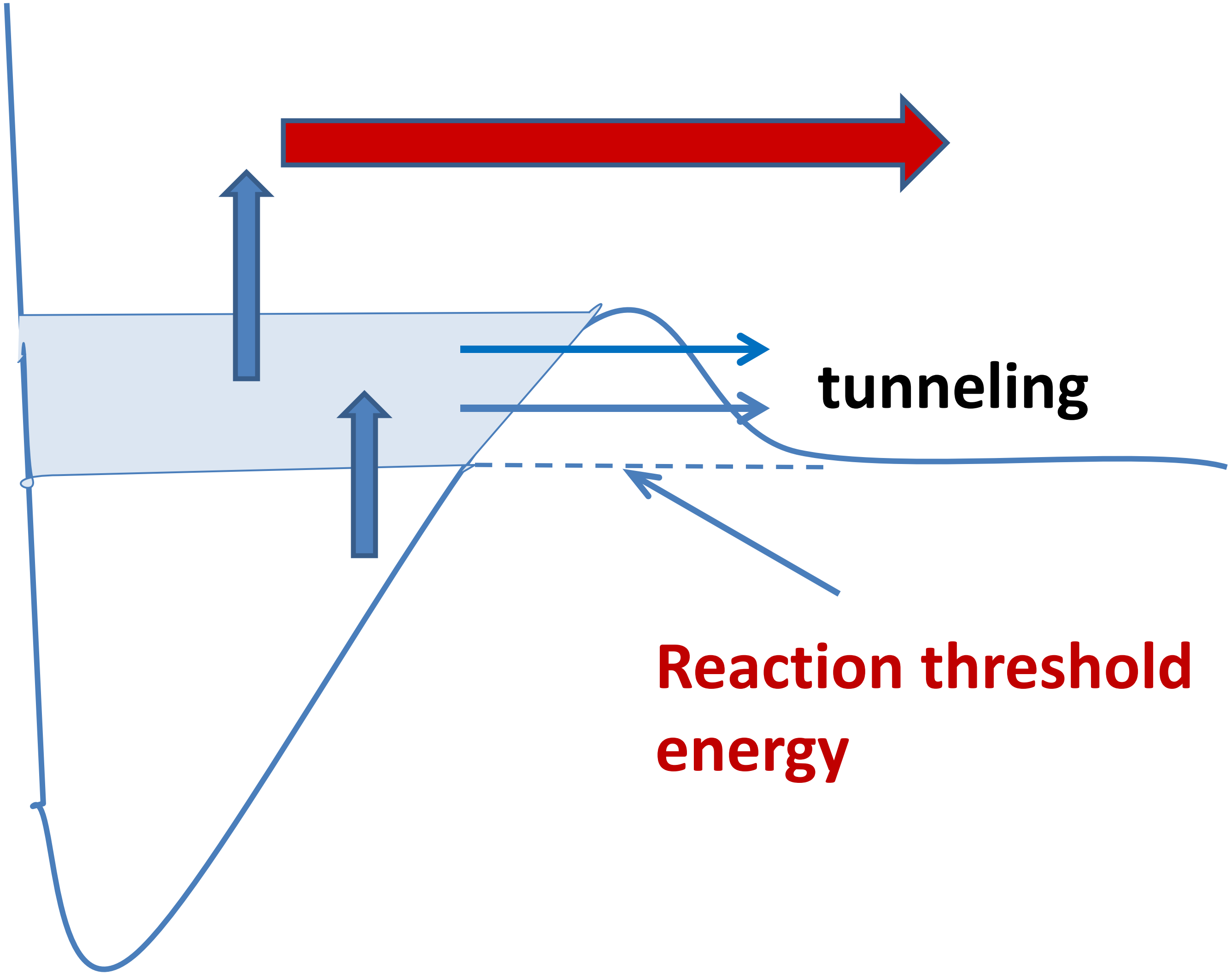
Timonen, et al 1987

Friedrichs ,et al 2002

Krasnoperov Helium collider

Yang, Tan, Carter, and Ju, U.S. National Meeting 2013

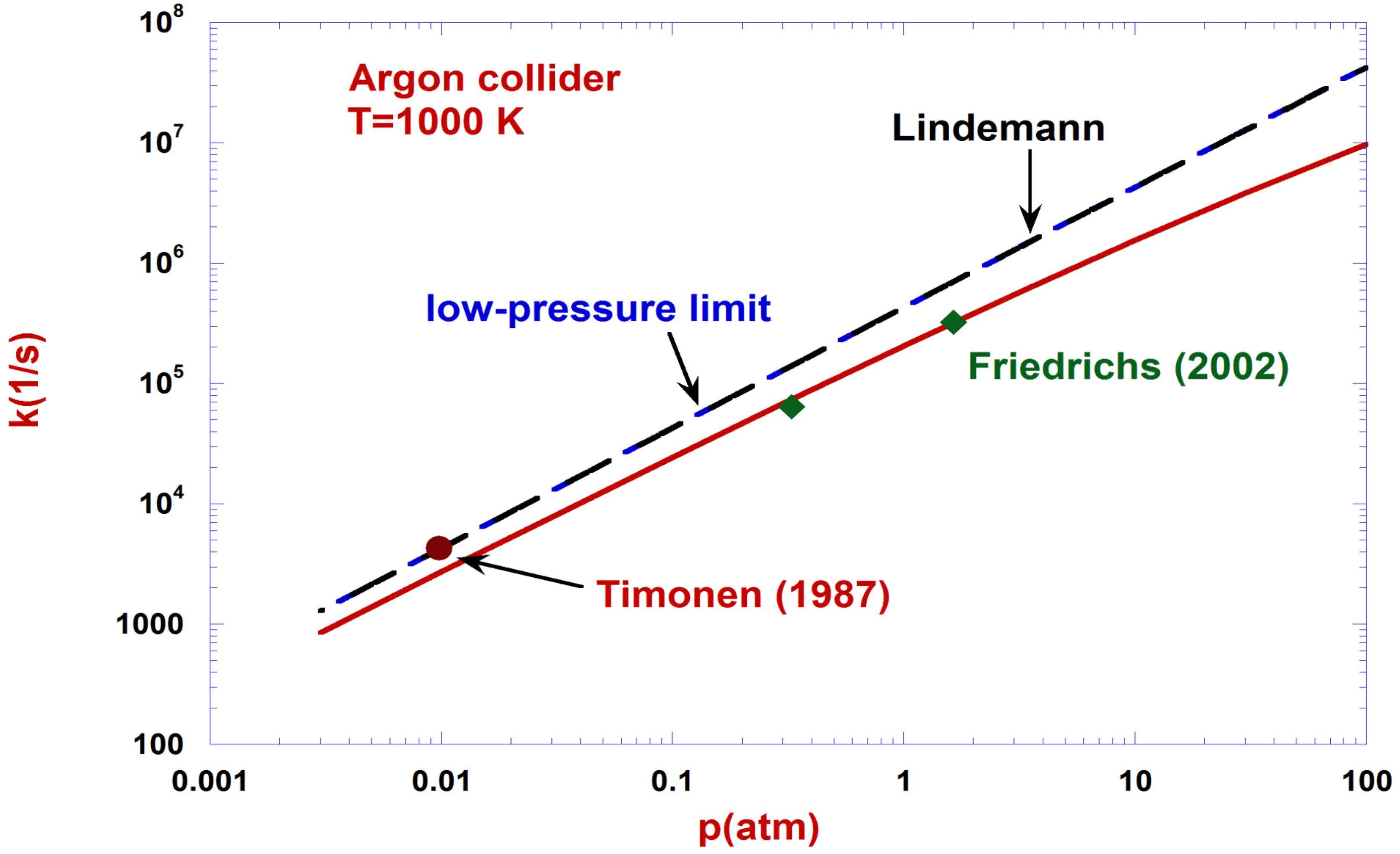
HCO dissociation



tunneling

Reaction threshold energy

HCO->H+CO



Yang, Tan, Carter, and Ju, U.S.
National Meeting 2013

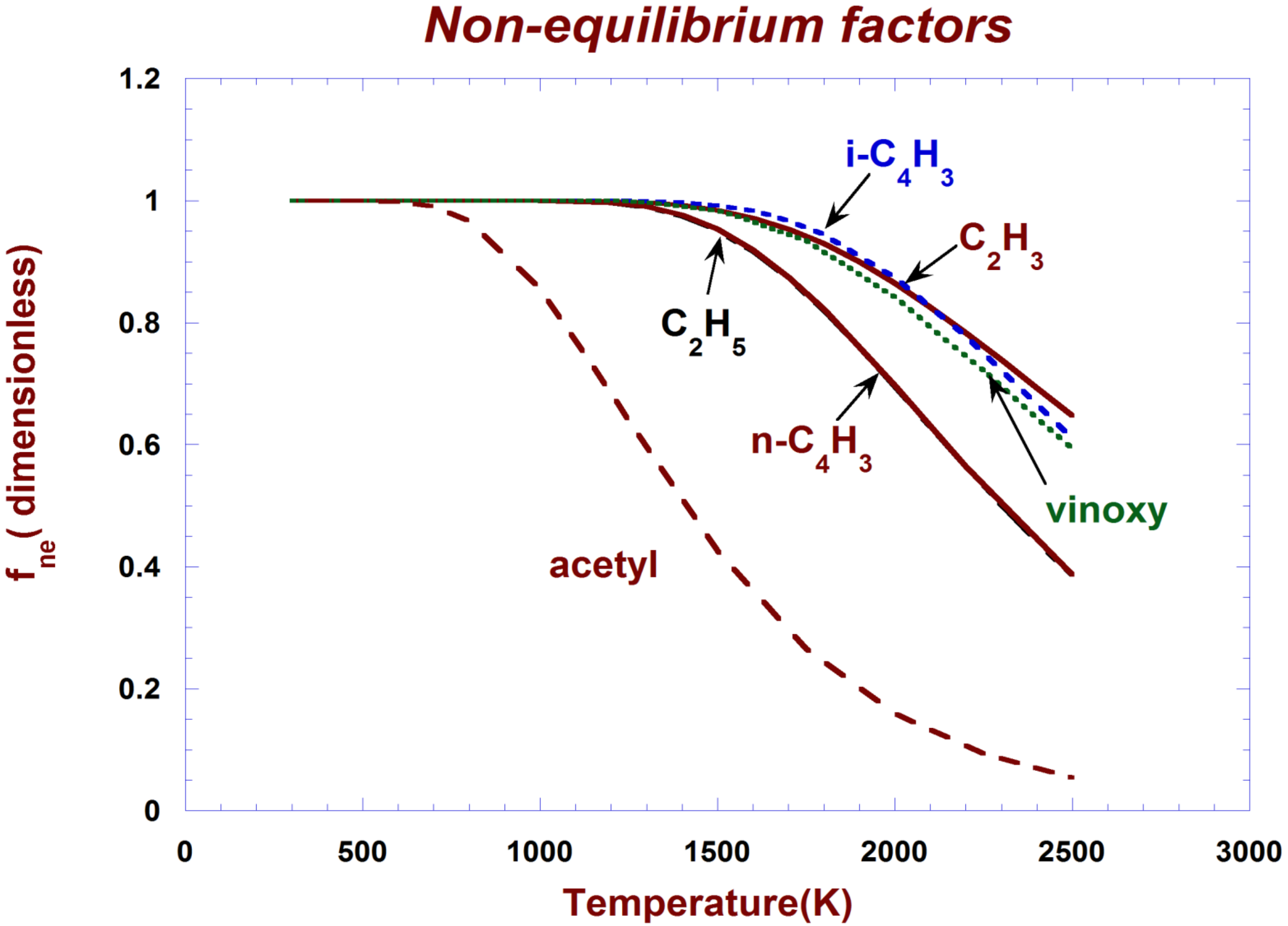
Non-equilibrium population distributions during dissociation of weakly-bound free radicals

- Non-equilibrium factor, f_{ne}, occurs naturally in the analytical treatment of reversible dissociation

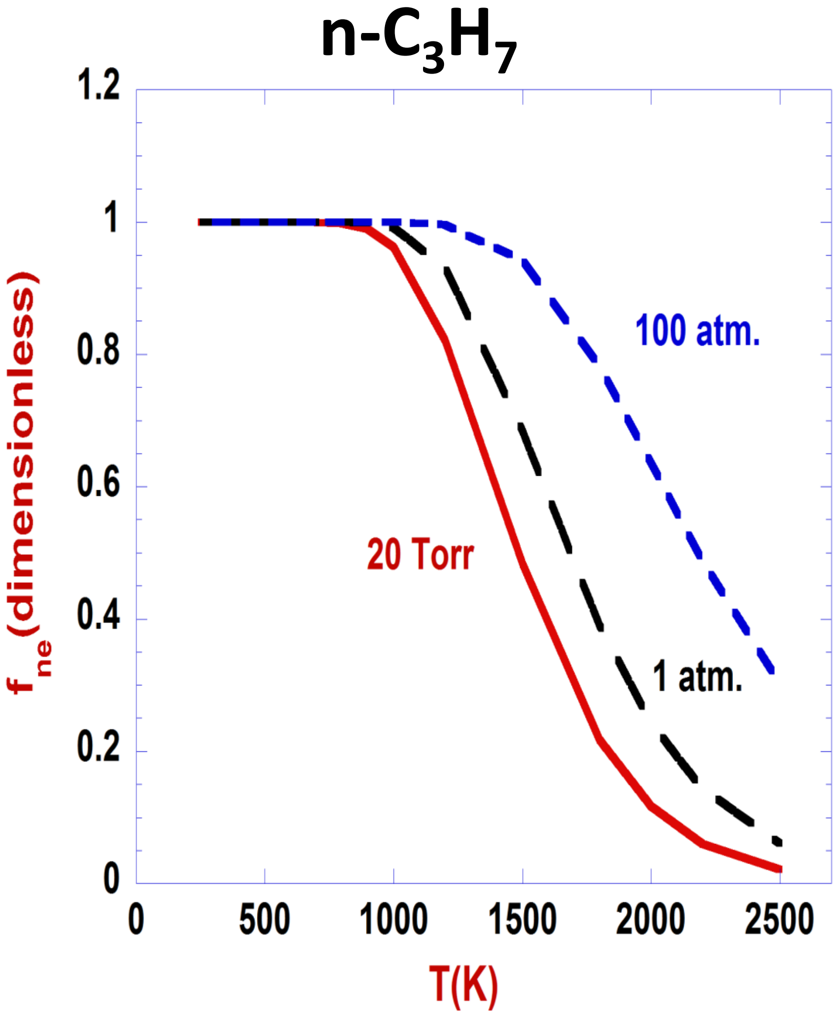
$$f_{ne} = 1 / \left[\int_0^\infty \frac{x(E)}{F(E)} x(E) dE \right]$$

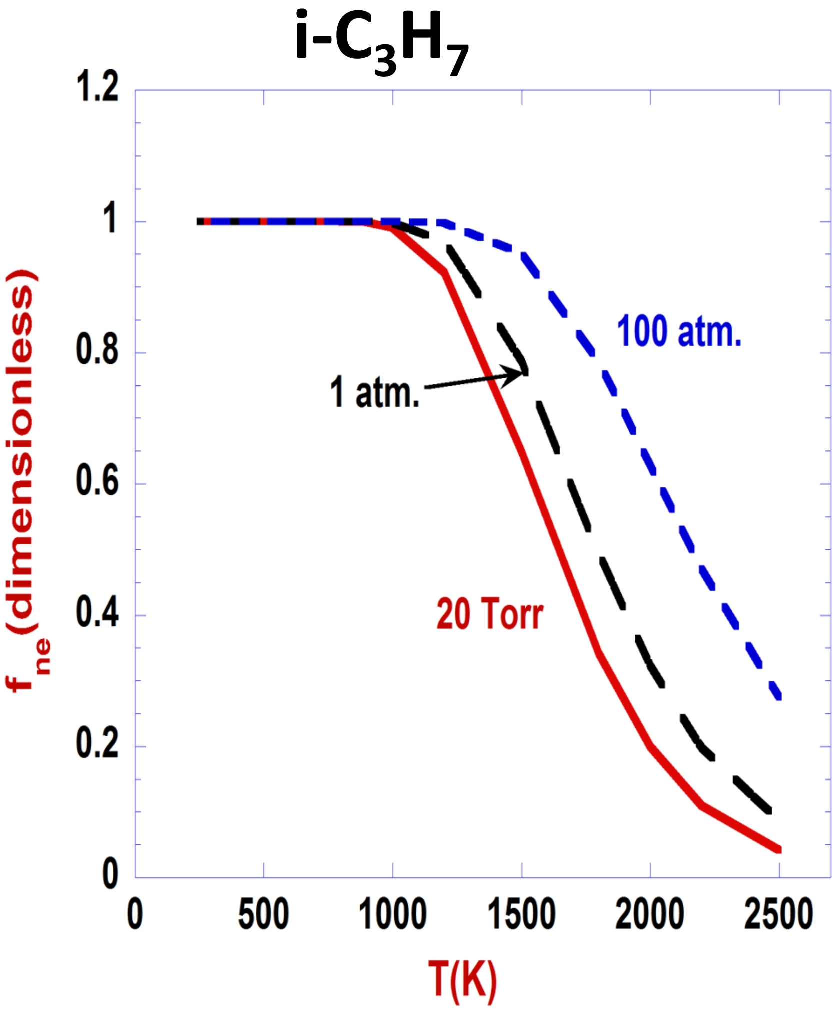
- Measure of the extent to which dissociation "disturbs" the equilibrium population distribution
- If f_{ne} is significantly smaller than 1, get significant disturbance ⇒ dissociation during vibrational relaxation ⇒ inadequacy of phenomenological (rate constant) description

Non-Equilibrium factors for Selected Radicals



Propyl radicals





Possible Solution

- **Internal energy relaxation is presumed to be infinitely fast in phenomenological models**

↓

- **Dissociated radical is formed before "thermalization" is complete**

↓

- **Take dissociated radical to be formed from radical-producing reactions, e.g.**

$$C_2H_6+OH \rightleftarrows C_2H_5+H_2O$$

$$C_2H_6+OH \rightleftarrows C_2H_4+H+H_2O$$

Reactions Investigated (or Re-Investigated) for this Project

Everything on C_3H_7 potential, …C_3H_6 …,… C_3H_5O…, …C_2H_4…,C_2H_5+H, C_2H_5+OH,C_2H_5+O_2,C_3H_7+O_2,C_3H_3 dissociation, $^3CH_2$+O_2, HCO+OH, CH_2OH/CH_3O dissociation,C_2H_3+O_2, dissociation of hydroxypropyl and propoxy radicals, etc. (probably a number that I have forgotten)

CH_3+OH⇄products

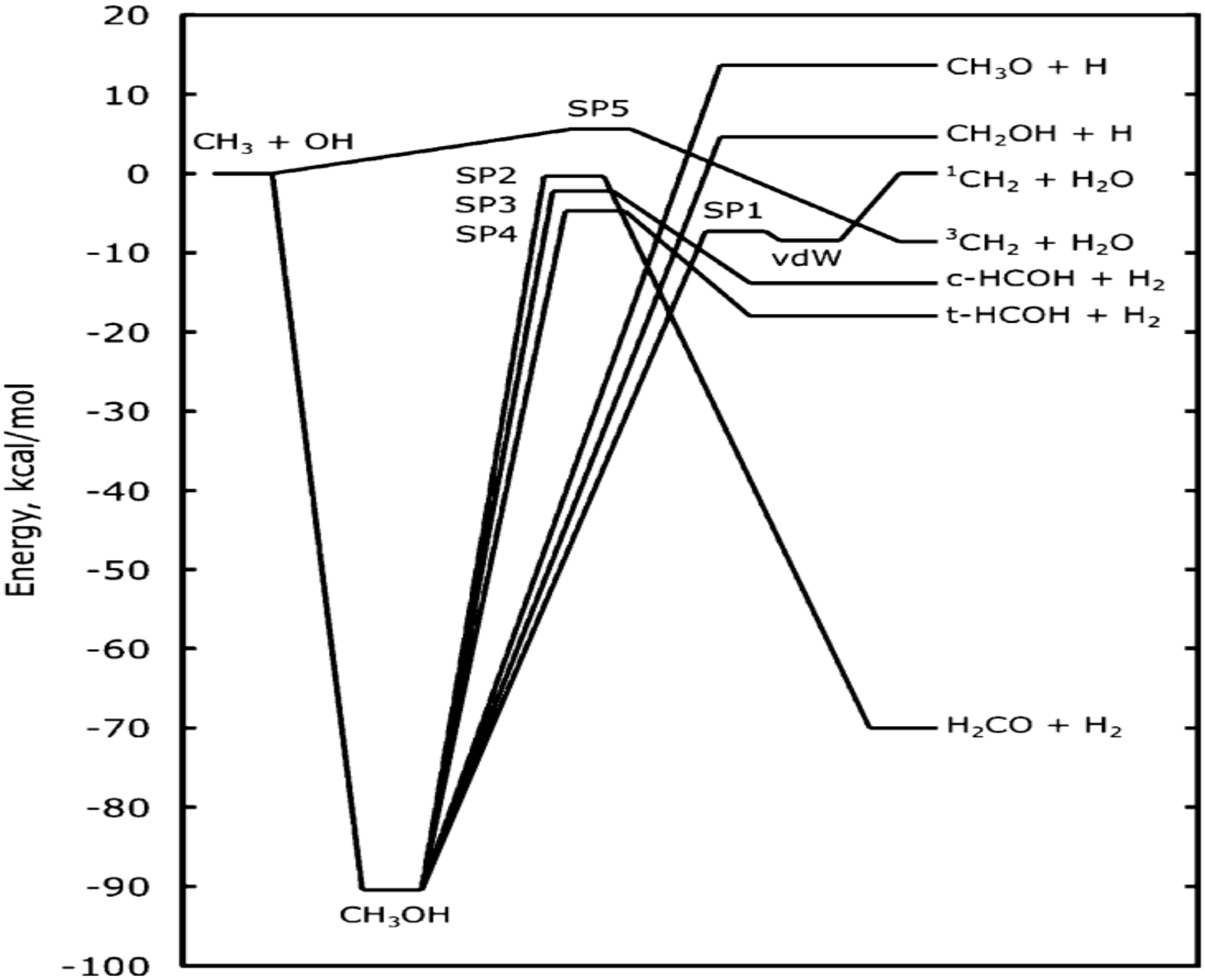
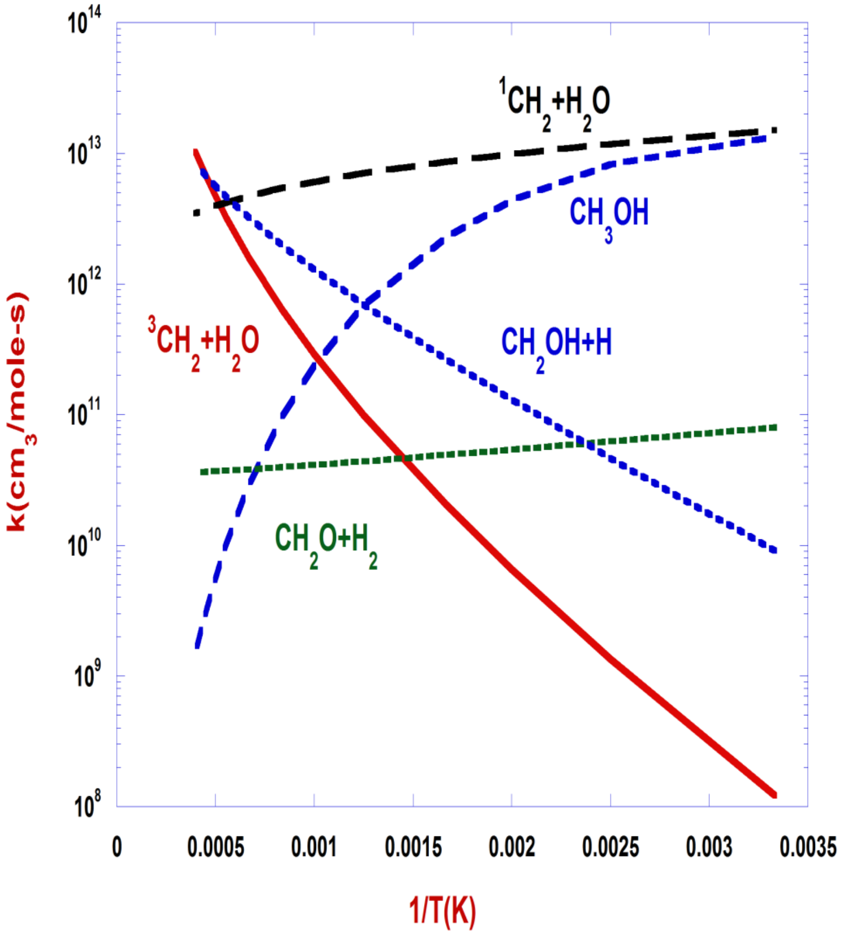
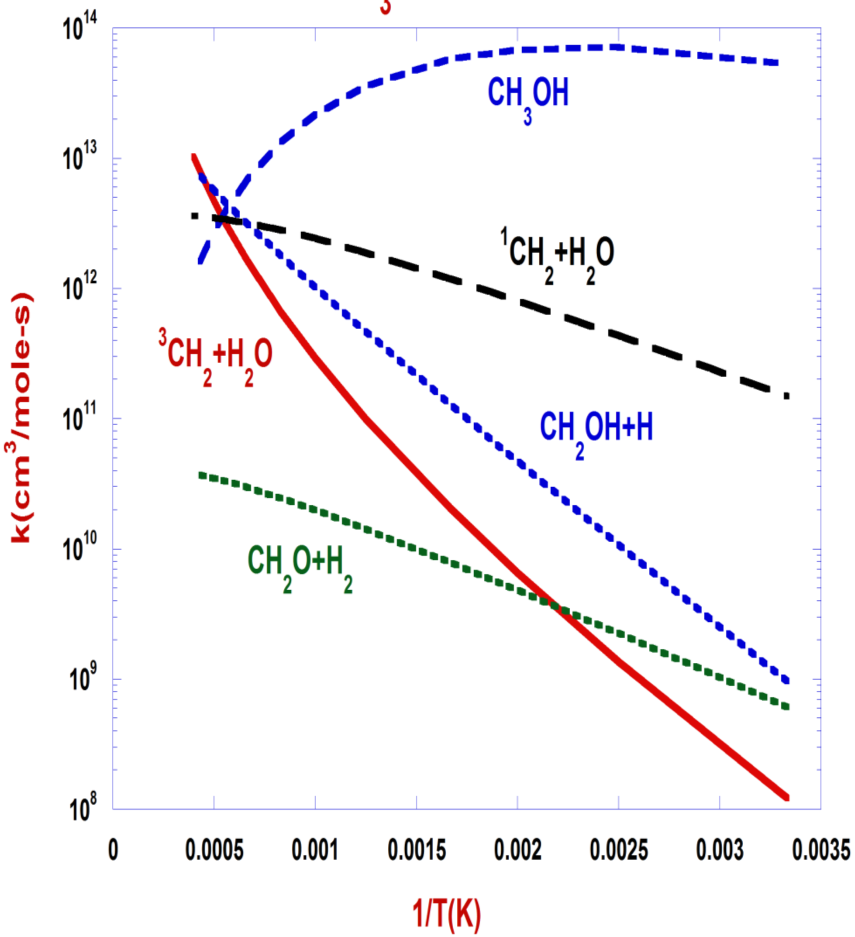


Figure 1. Zero-point inclusive stationary point energies computed at the QCISD(T)/CBS//B3LYP/6-311++G** level of theory.

CH_3+OH⇄products



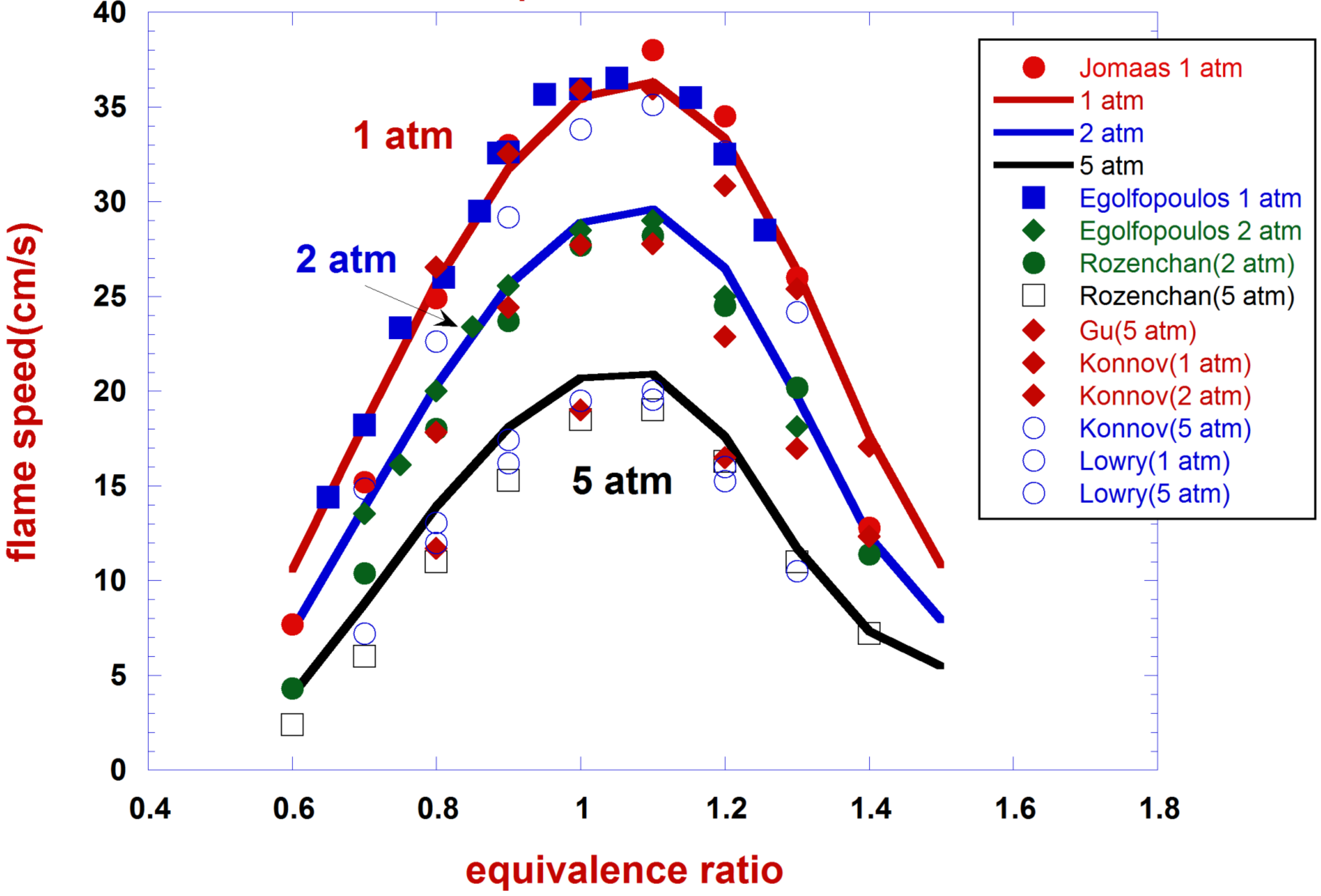
CH3+OH 10 Torr



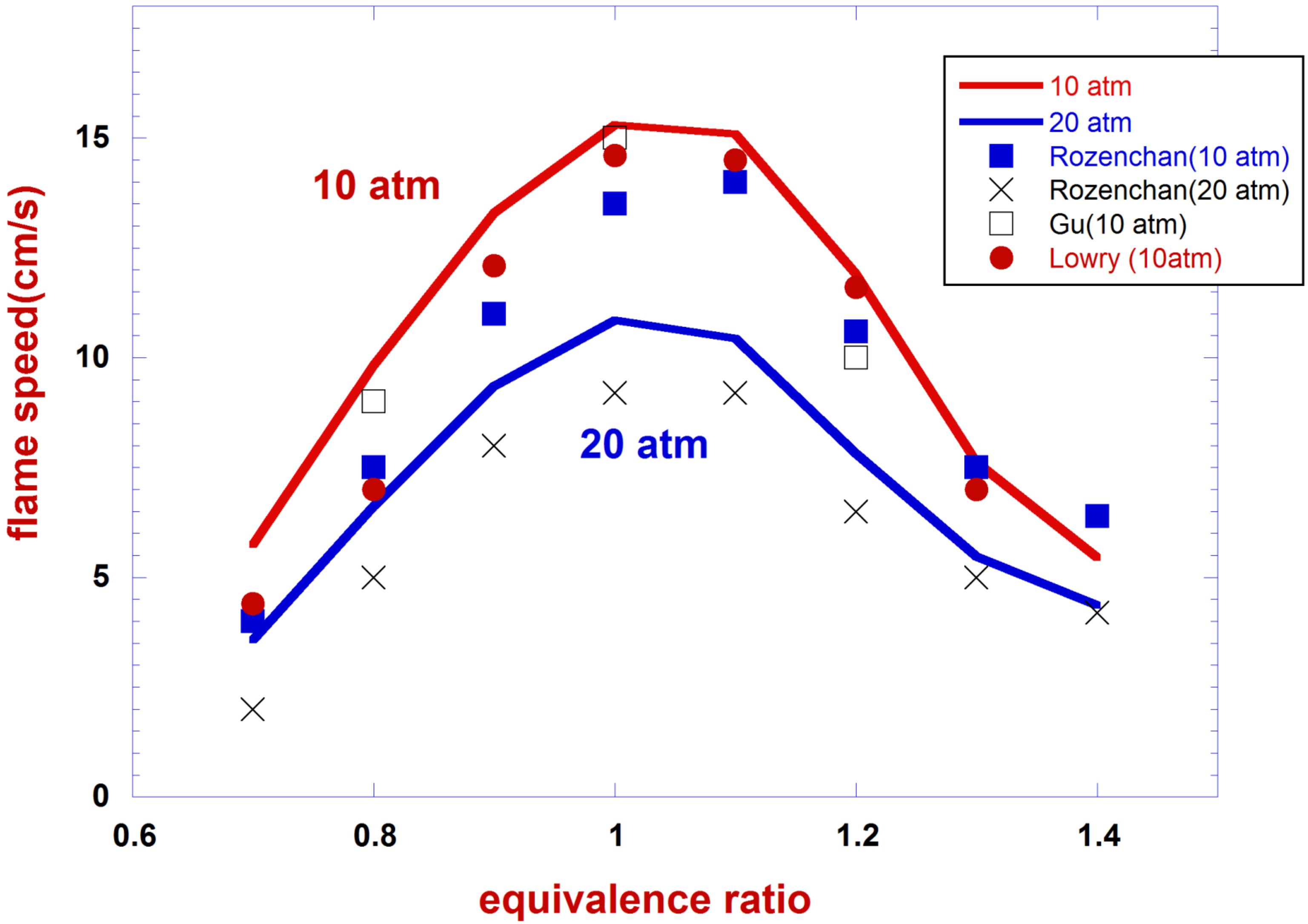
CH_3+OH 13.2 atm

Comparison with Experiment

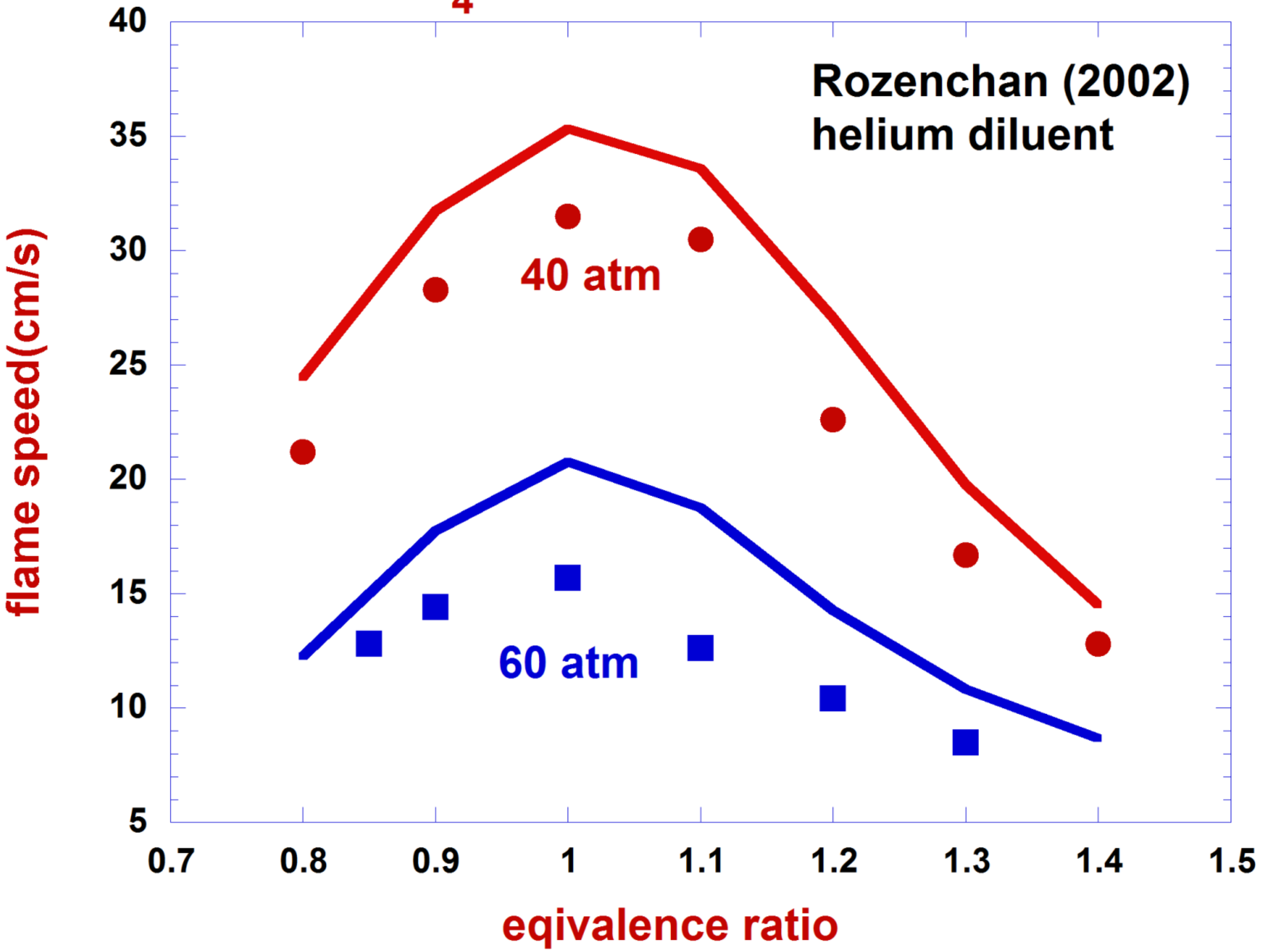
CH_4 flame speeds



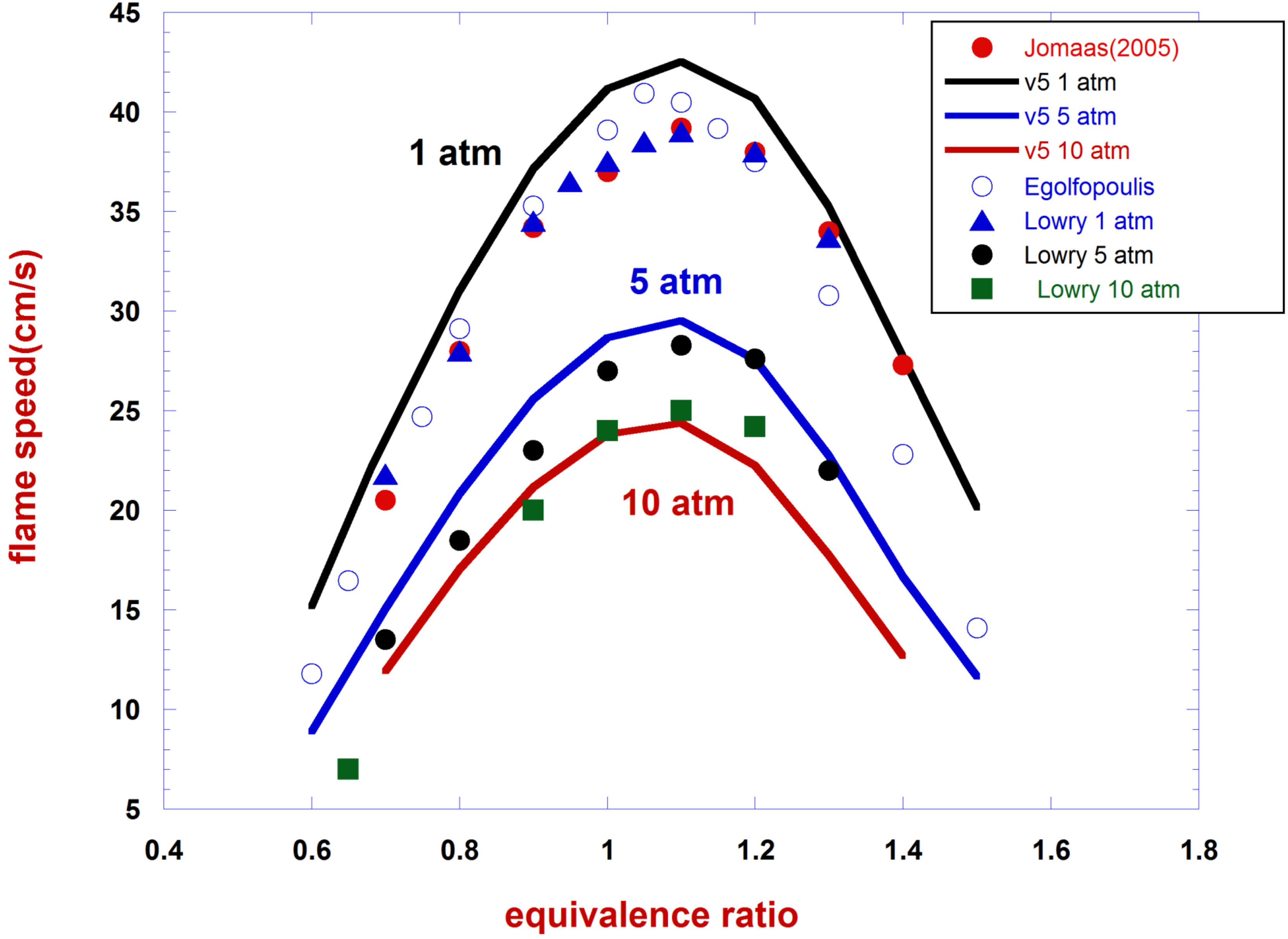
CH_4 flame speeds



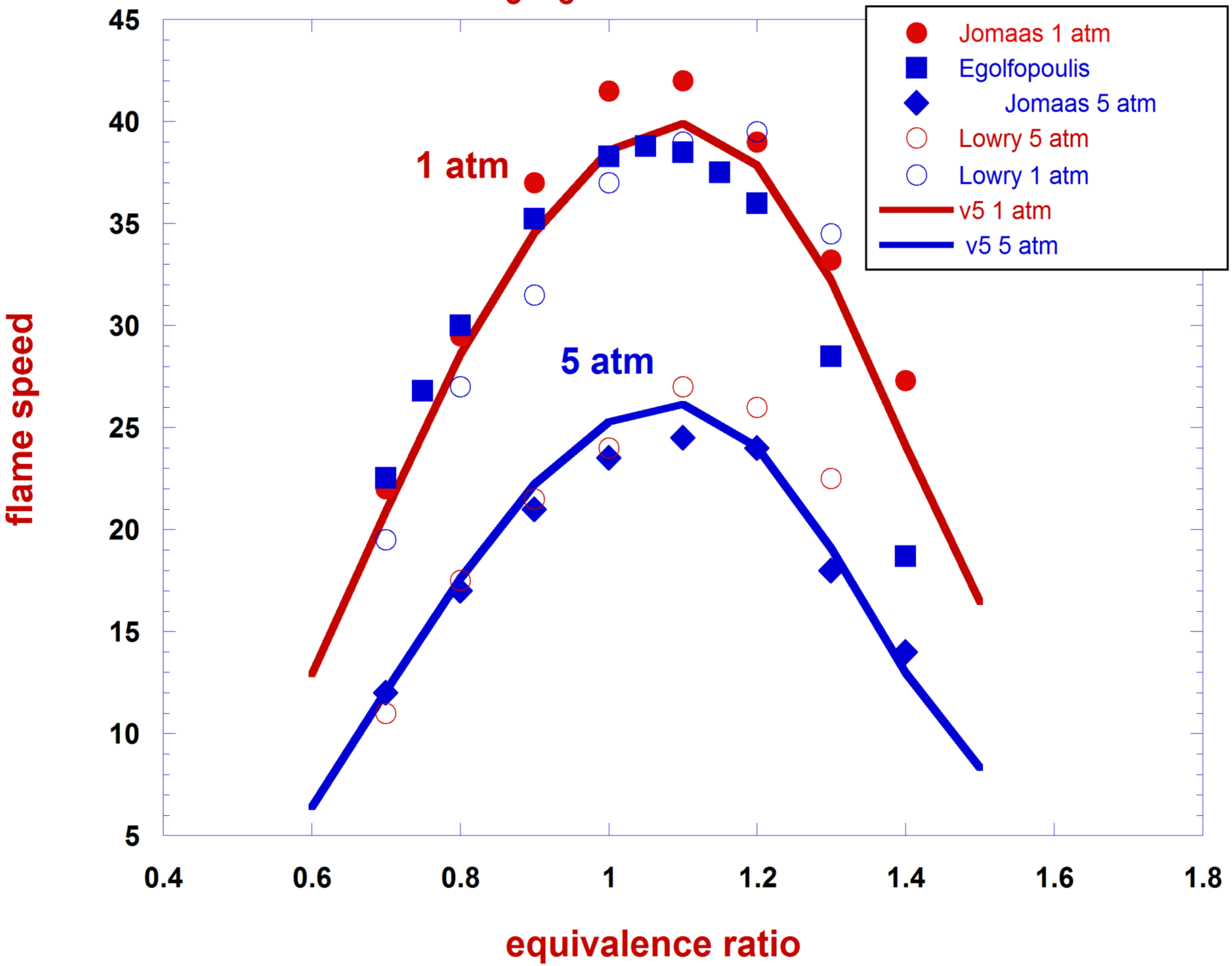
CH_4 ultra-high pressure



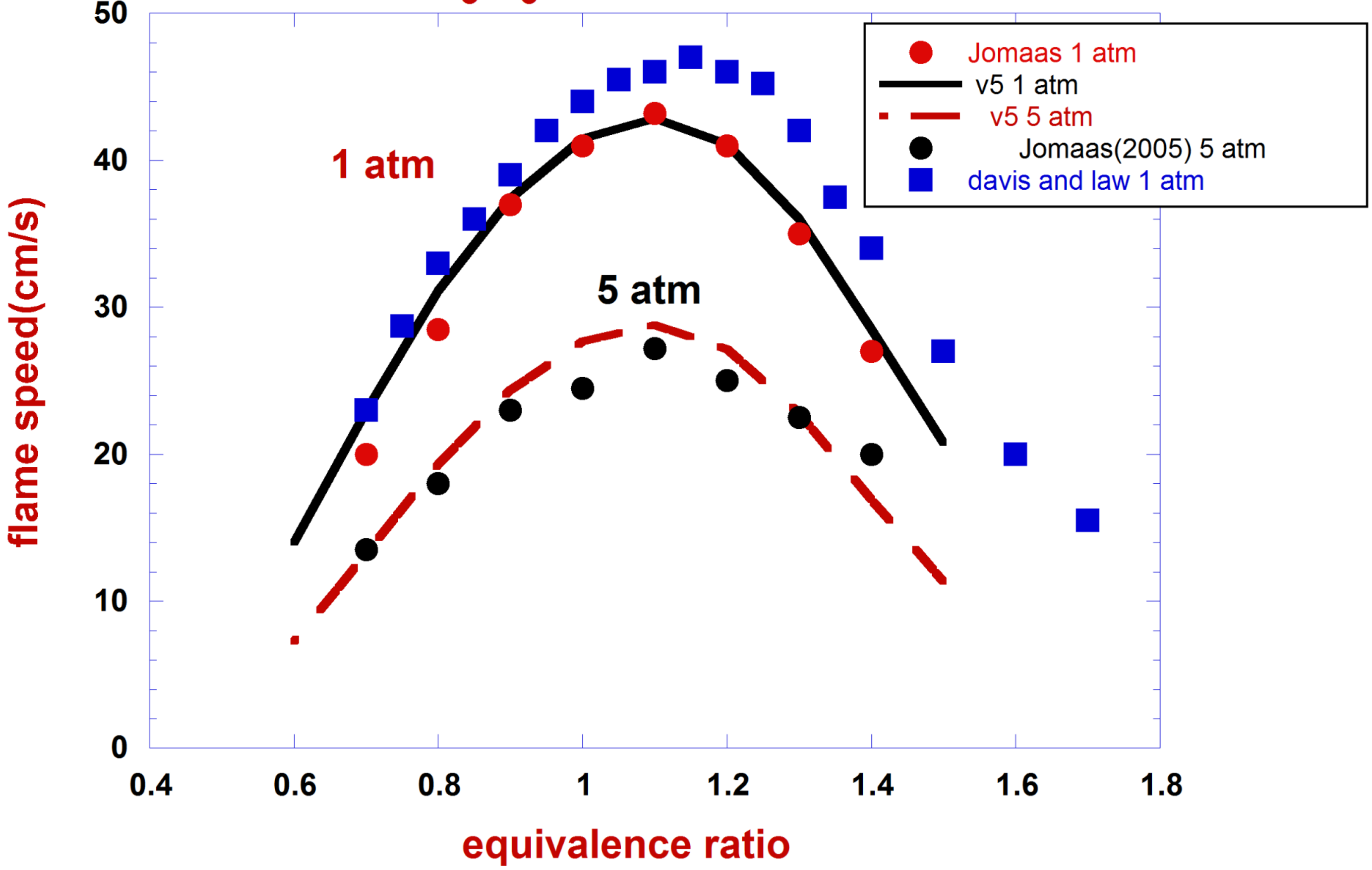
C_2H_6 flame speeds



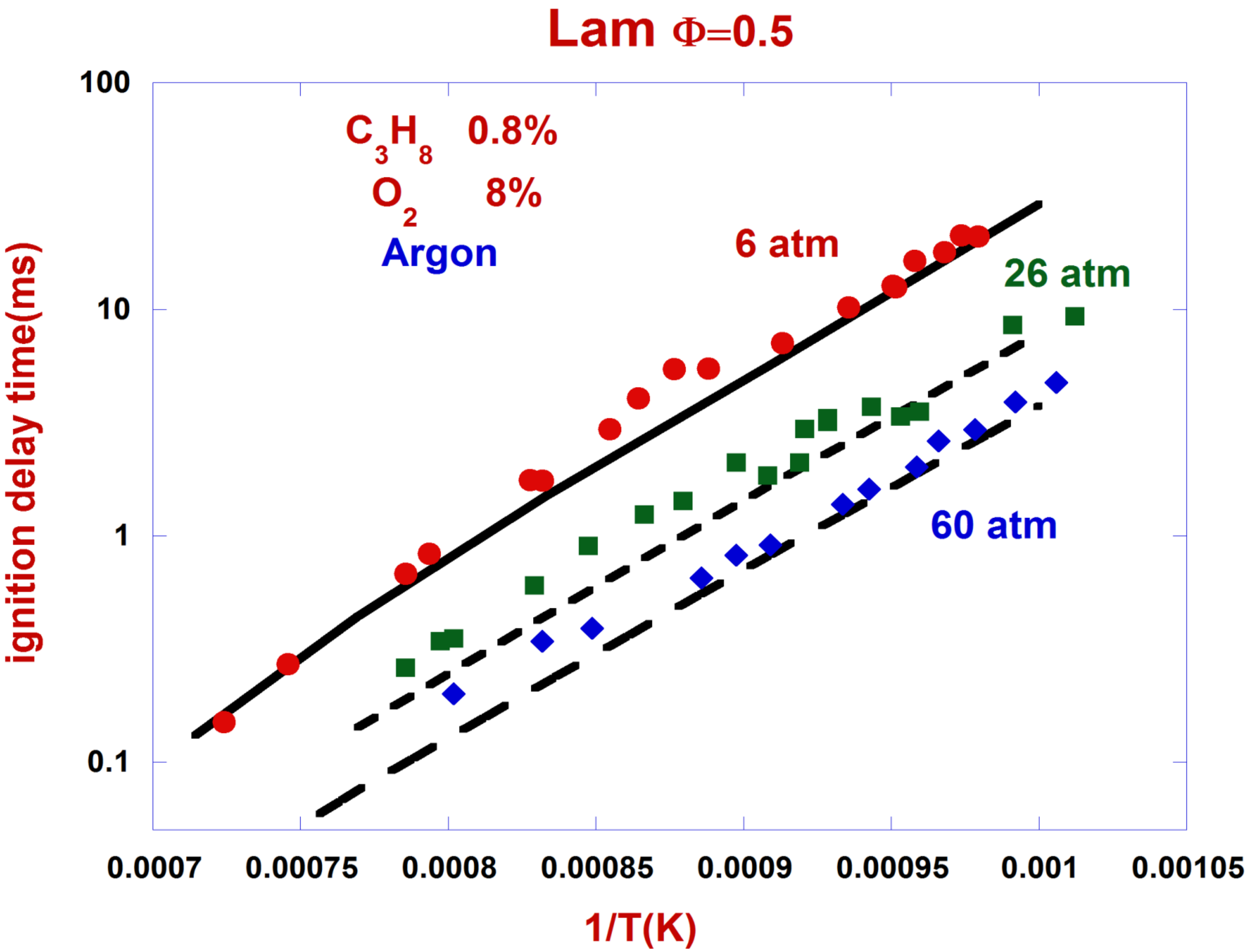
C_3H_8 flame speeds



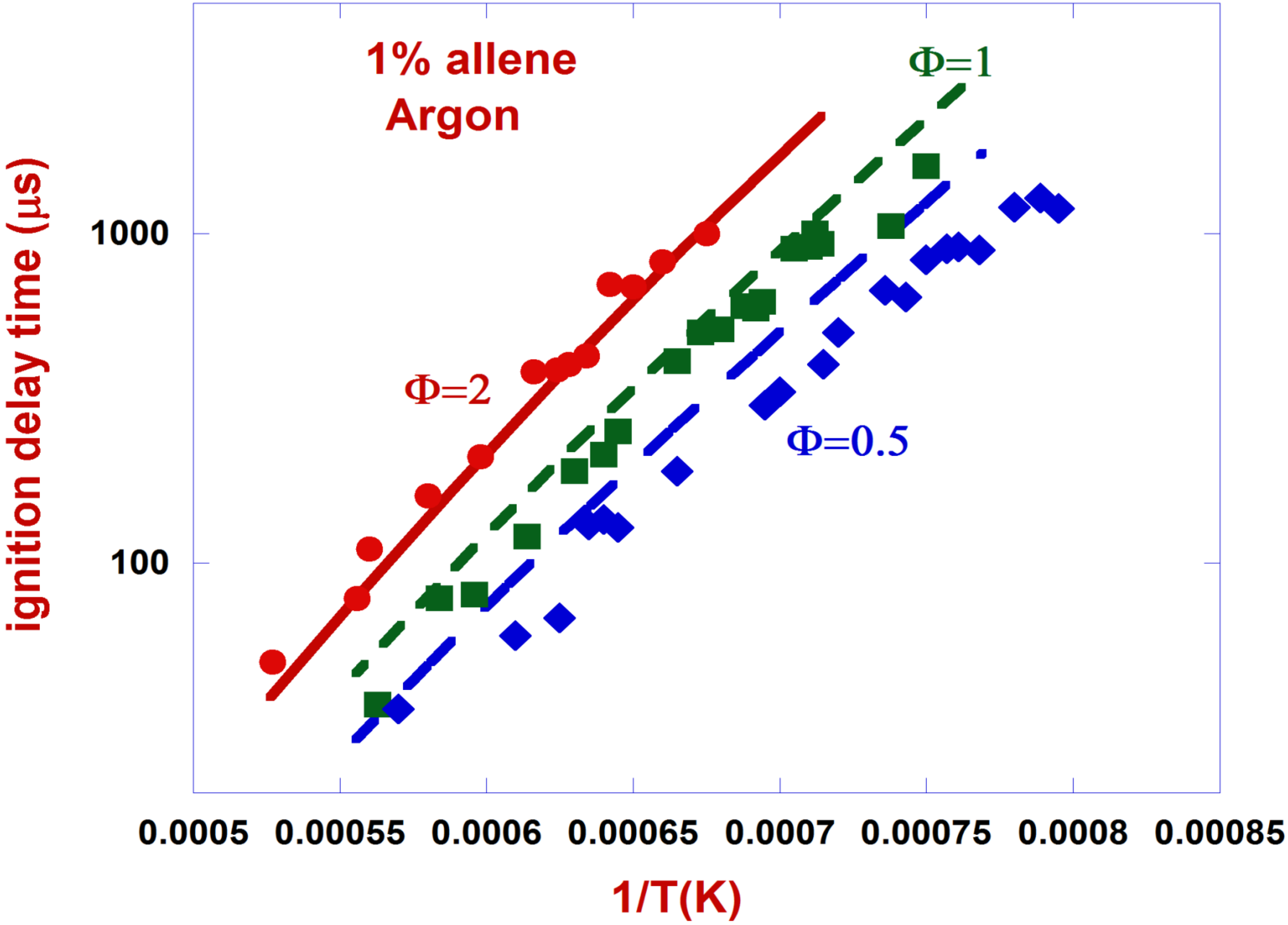
C_3H_6 flame speeds



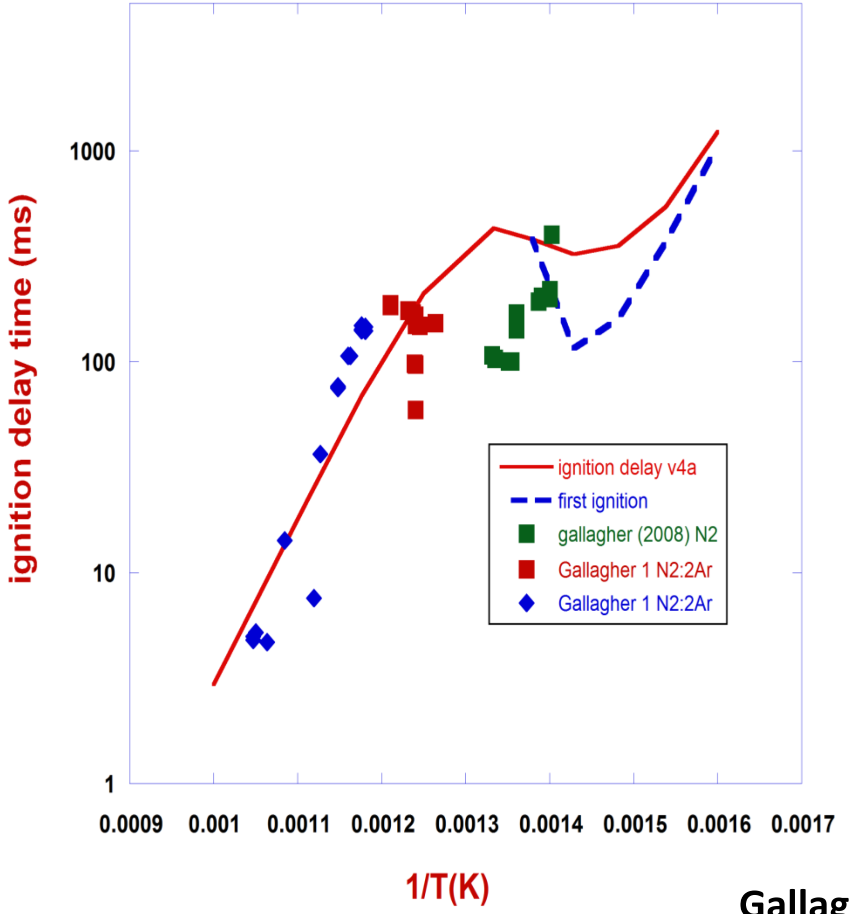
Propane Ignition Delay Times

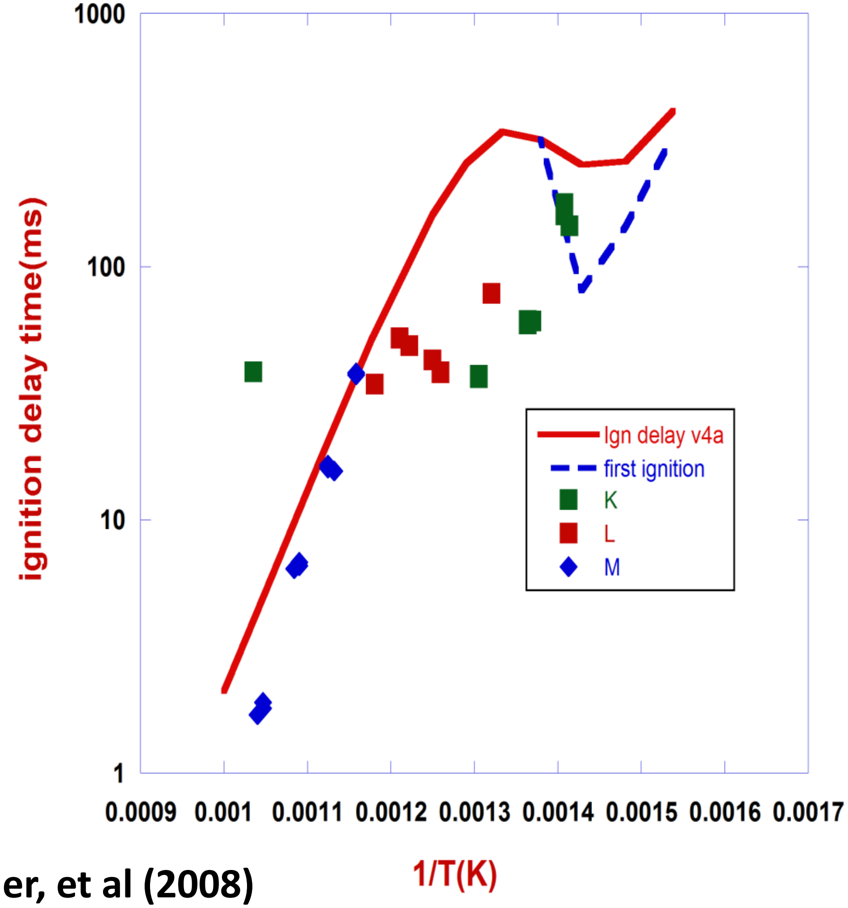


Allene ignition delay times



Low-Temperature Autoignition of Propane


Low T ignition $\Phi=0.5$


Low T ignition $\Phi=1.0$

Gallagher, et al (2008)