Predictive Theoretical Kinetics and Predicting Its Future in Combustion Research

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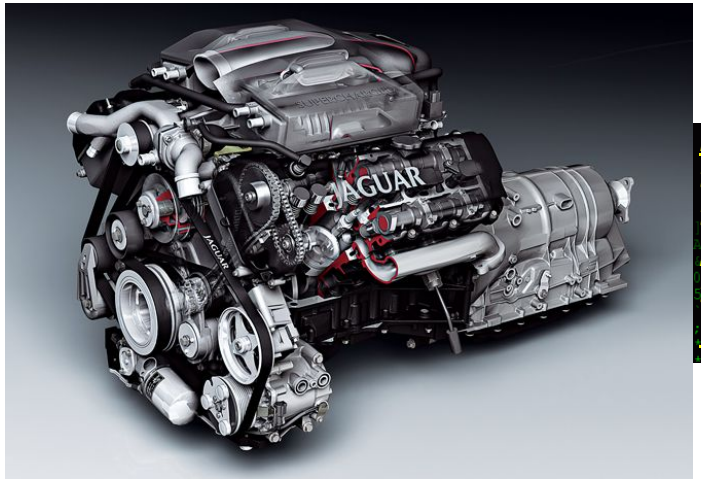
CRF RHS
2/16/12

Why do we study kinetics?

Predicting the internal combustion engine (PreSICE)



Physics
transport, heat transfer, surface interactions, turbulence, mixing
Chemistry

kinetics ≈ chemistry

$$H + O_2 \xrightarrow{k_1(T)} O + OH$$

$$H + O_2 \xrightarrow{k_2(T,P)} HO_2$$

branching → more radicals

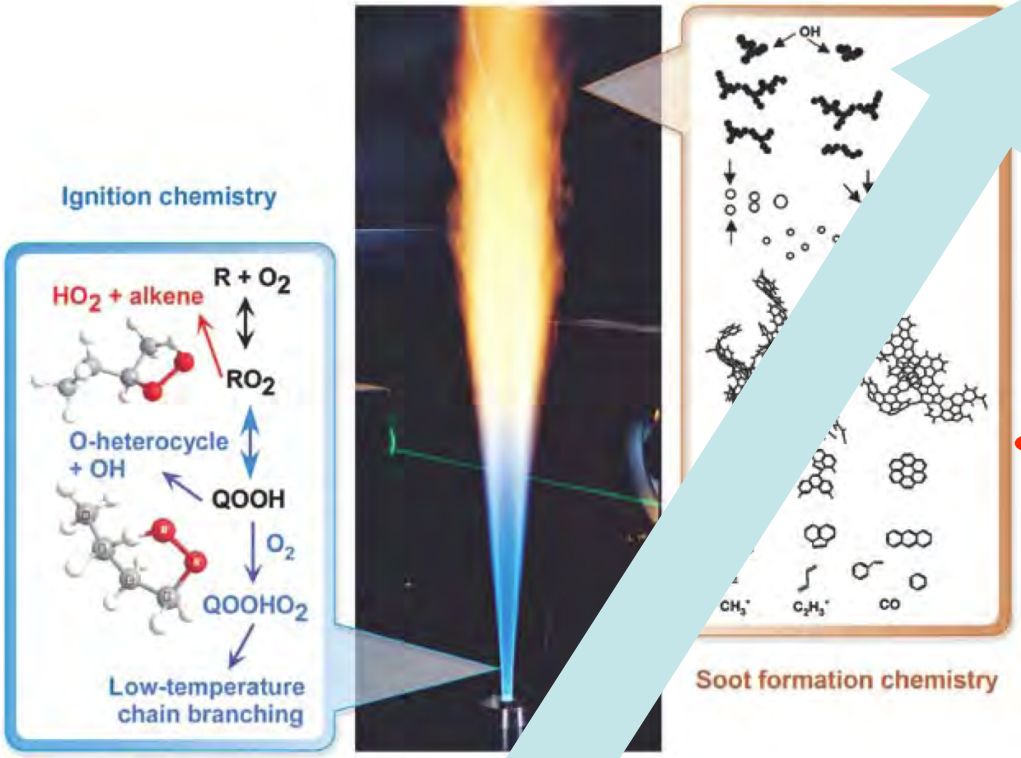
terminating → $H_2 + O_2$

rate = *k* [reactants]

Chemistry in combustion

From the PreSICE workshop report (3/3/11)

Where does chemistry matter in combustion?



$$\text{fuel} + O_2 \longrightarrow CO_2 + H_2O$$

Chemistry is modeled as a long list of reactions & rates

A+B=C+D	k(T,P)
OH+H2=H2O+H	2.144E8 1.52 3449.
O+OH=O2+H	2.57E13 -0.1589 -479.68
O+H2=OH+H	0.506E+05 2.670 6290.000
H+O2(+M)=HO2(+M)	5.8E11 0.6724 -290
	LOW / 7.2E20 -1.73 536 /
	TROE /0.72 1E-30 1E30 1E30/
	AR/0.5/ H2O/10/ CO2/2/ CH4/3/
OH+HO2=H2O+O2	1.9E16 -1.0 0.0
H+HO2=2OH	1.69E14 0.0 874.
H+HO2=H2+O2	4.28E13 0.0 1411.
H+HO2=O+H2O	3.01E13 0.0 1721.
O+HO2=O2+OH	3.25E13 0.0 0.0
2OH=O+H2O	4.331E3 2.7 -2485.7
CH3+OH=CH3OH	4.498E8 1.3 -54590

...

1000s of reactions

...

C3H8+C2H5=C3H7(i)+C2H6	1.51E+00 3.46 7470.0
C3H8+C2H5=C3H7(n)+C2H6	9.03E-01 3.65 9140.0
C3H8+CH2CHCH2=C3H6+C3H7(n)	2.35E+02 3.3 19842.0
C3H8+CH2CHCH2=C3H6+C3H7(i)	7.83E+01 3.3 18169.0
C3H7(n)(+M)=C2H4+CH3(+M)	1.23E+13 -0.1 30202.0

...

...

Joint theory/experiment kinetics

CRF/Argonne approach

Single-reaction kinetics

experiments anchor theory

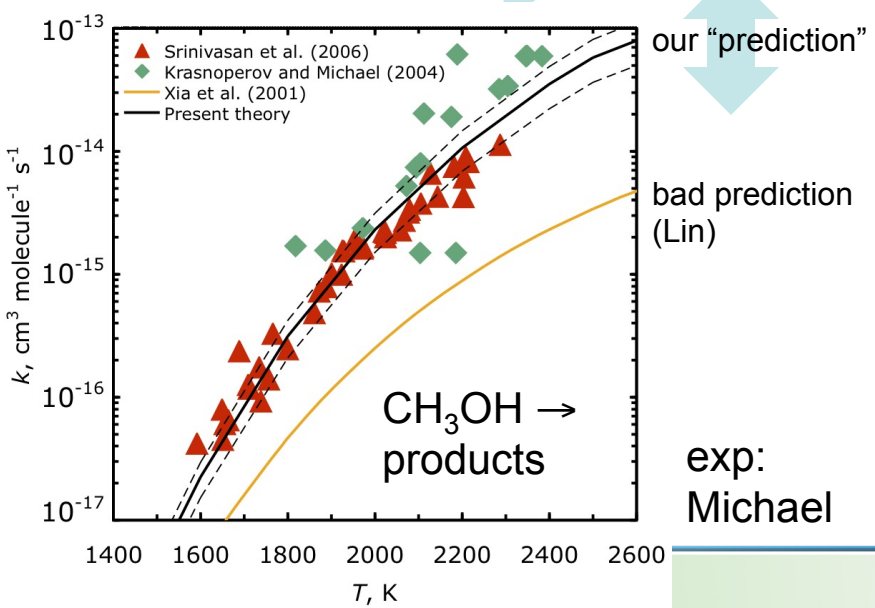
theory extrapolates beyond exp T & P

Detailed chemical mechanisms

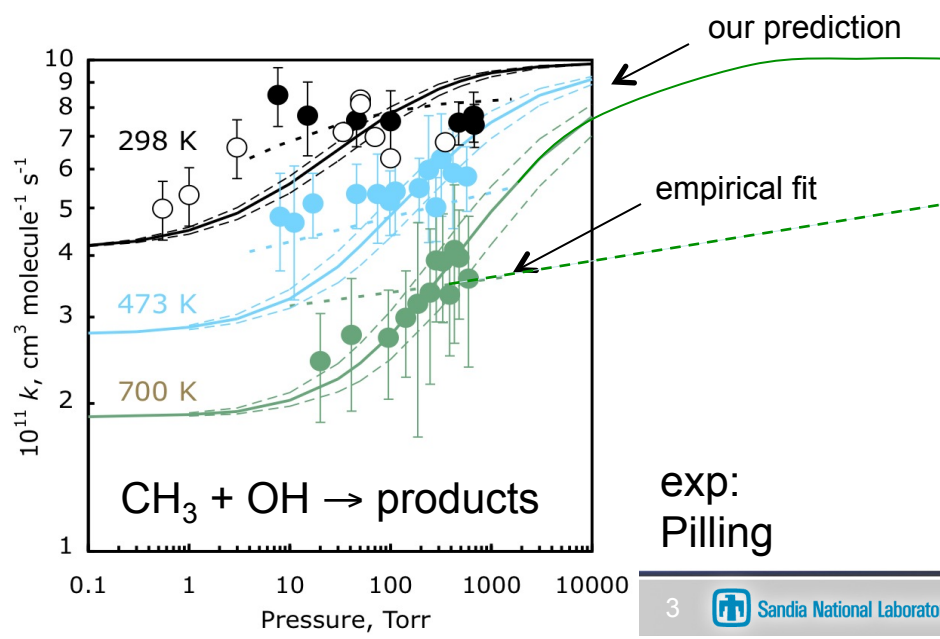
experimental vs modeled

flame structures

autoignition
NOx
benzene/soot



exp: Michael

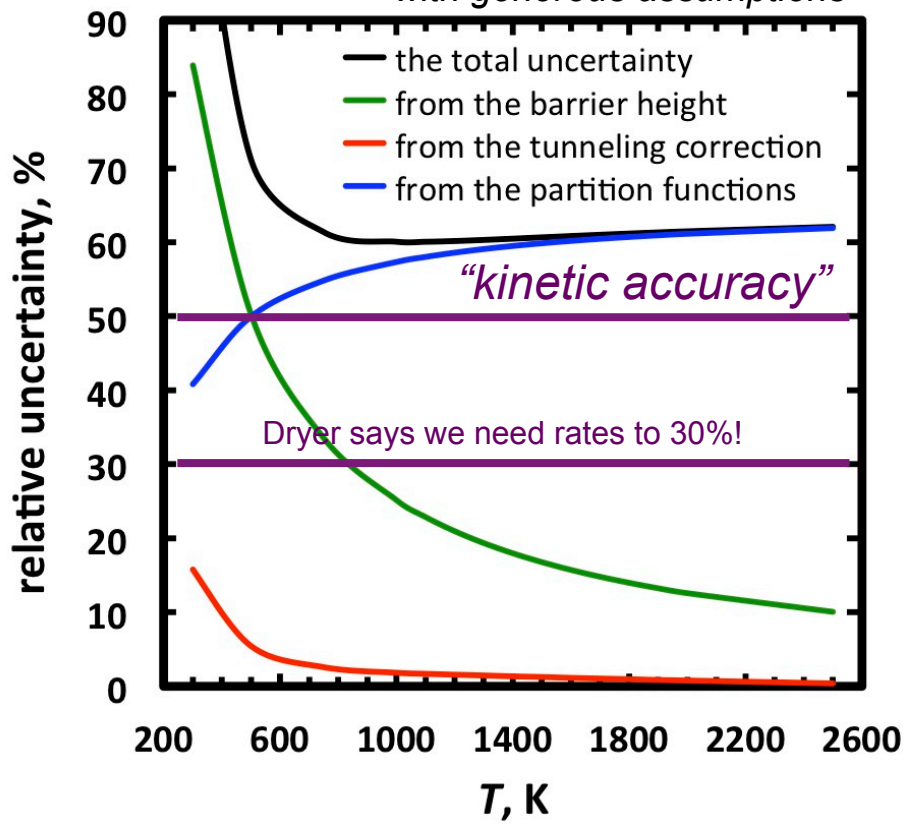


exp: Pilling

How accurate is theoretical kinetics?

For a reaction with a barrier

with generous assumptions



tunneling

barrier height

$$k_{\mathrm{TST}}(T) = \kappa \frac{k_B T}{h} \frac{Q^{\neq}}{Q_r} e^{-V^{\neq}/k_B T}$$

partition functions (frequencies, rotational constants)

$$\frac{\sigma_k^2}{k_{\mathrm{TST}}^2} = \frac{\sigma_\kappa^2}{\kappa^2} + \frac{\sigma_{Q^{\neq}/Q_R}^2}{(Q^{\neq}/Q_R)^2} + \frac{\sigma_{V^{\neq}}^2}{(k_B T)^2} \quad (\pm \text{ cov.})!$$

Challenge #1 for predictive theory

Vibrational anharmonicity in Q

dominates the error at combustion *T*

New CRF initiative with Eugene Kamarchik: High Performance Computing + Monte Carlo

Not shown:

Challenge #2: *Pressure dependence*

Challenge #3: *Spin-forbidden chemistry (new)*

Challenge #2: Pressure dependence

Predictive models for collisional energy transfer

with Melania Oana and Jim Miller

- Collisions stabilize/activate intermediates
- In the high pressure limit

  $k_{TST} << k_{collisions}$

  The TS is rate limiting

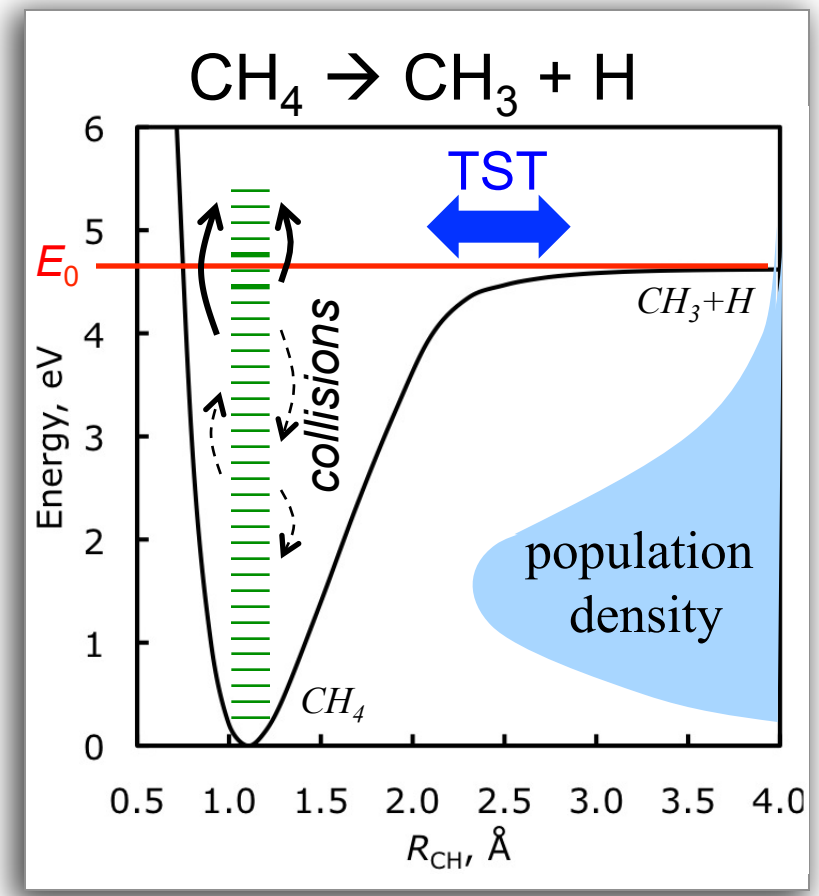
  Lots of good methods for this limit
- In the low pressure limit

  $k_{TST} >> k_{collisions}$

  Threshold collisions are rate limiting

  No quantitative methods for this limit
- At intermediate pressures

  Both effects are important



Predicting collisional energy transfer using classical trajectories

Energy transfer model

- $k_{collision}$ α Z(T) x P(E ← E')

  collision rate x distribution of outcomes
- simple models for Z and P
- need $\langle \Delta E_d \rangle$, average energy in downward collisions
- previous work was not quantitative or empirical

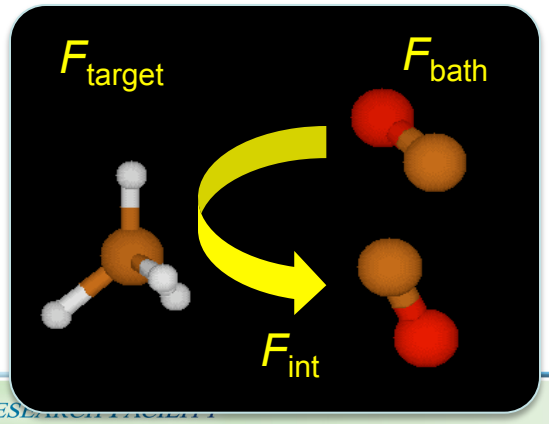
Quantitative $\langle \Delta E_d \rangle$ with good forces

- "Direct" dynamics

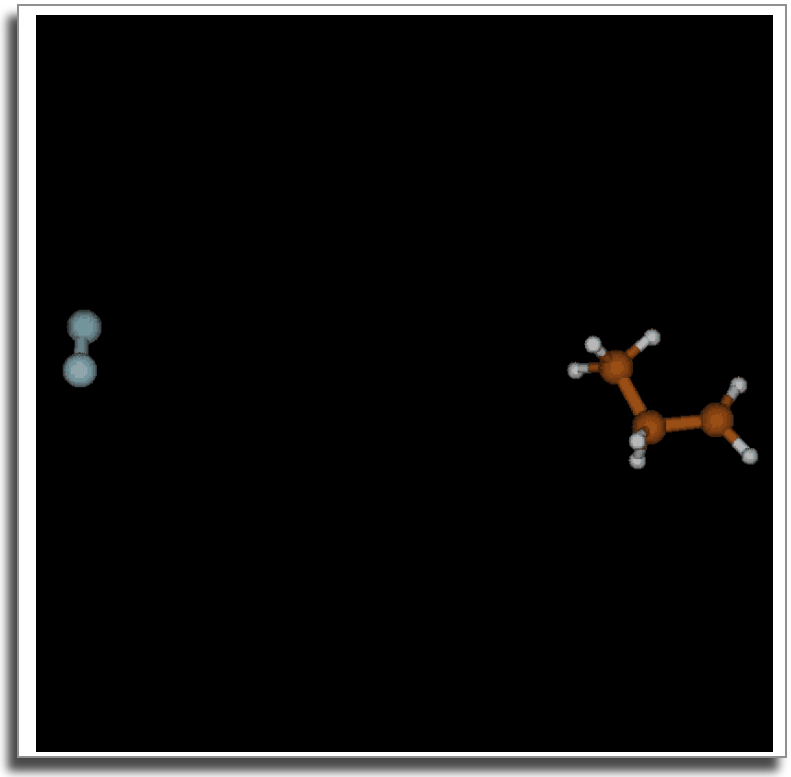
  Very expensive & accurate
- Semiempirical

  Parameterized & cheap

complementary approaches

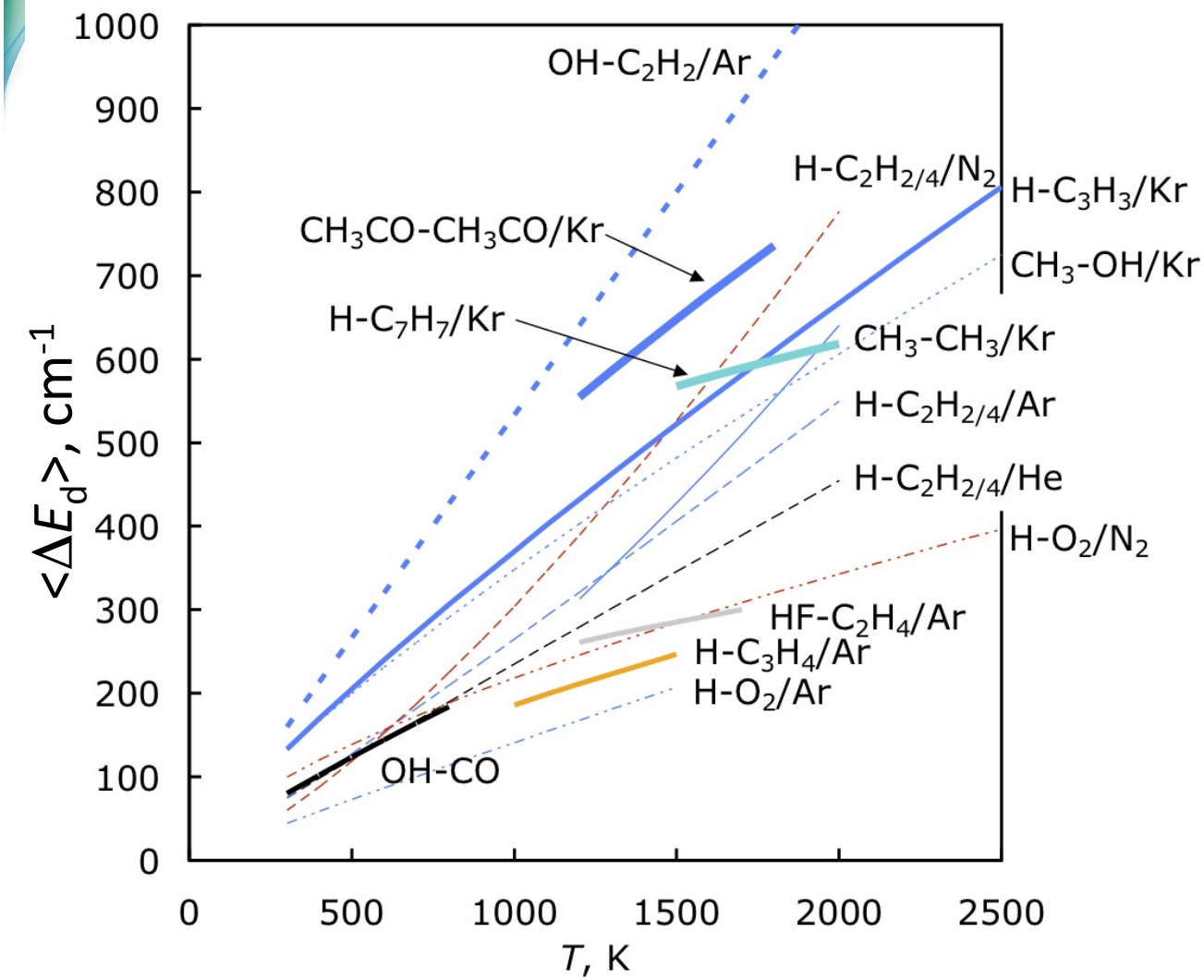


n-propyl + N_2



Empirical energy transfer parameters

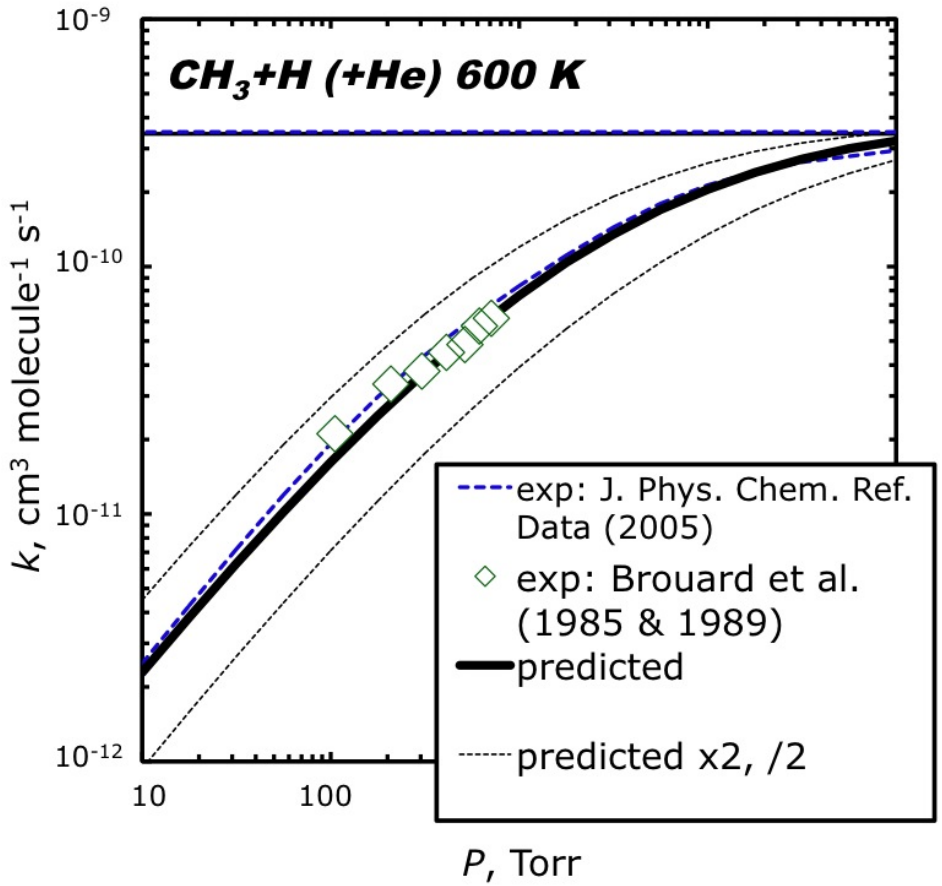
Previous approach

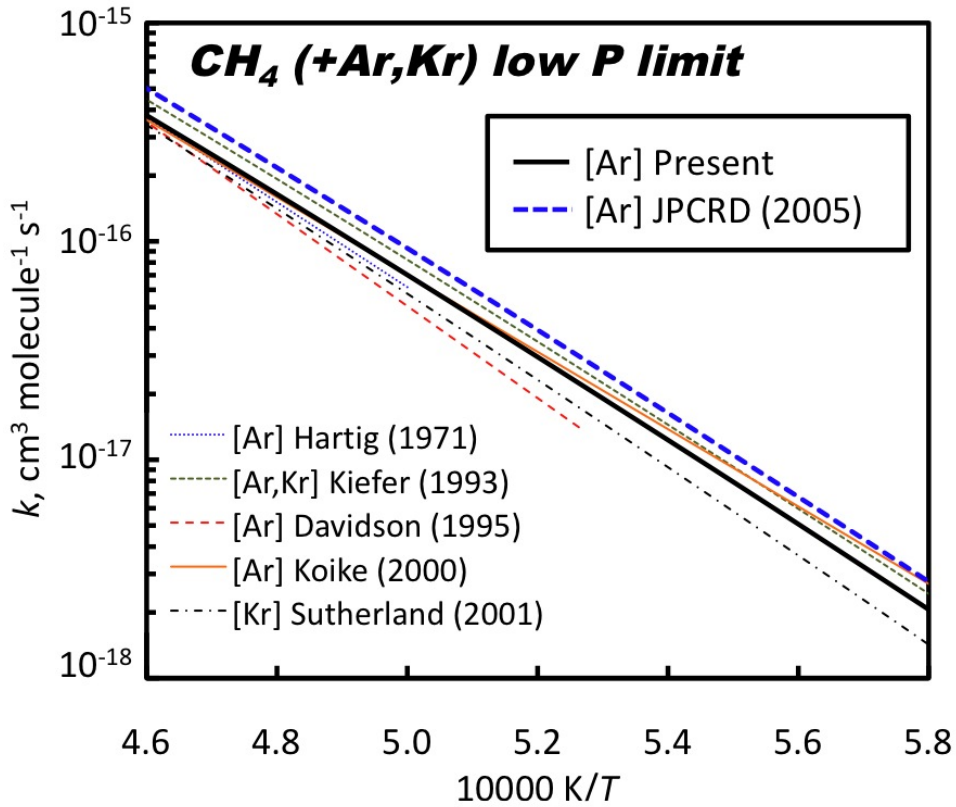


no clear trends

Calculated energy transfer parameters

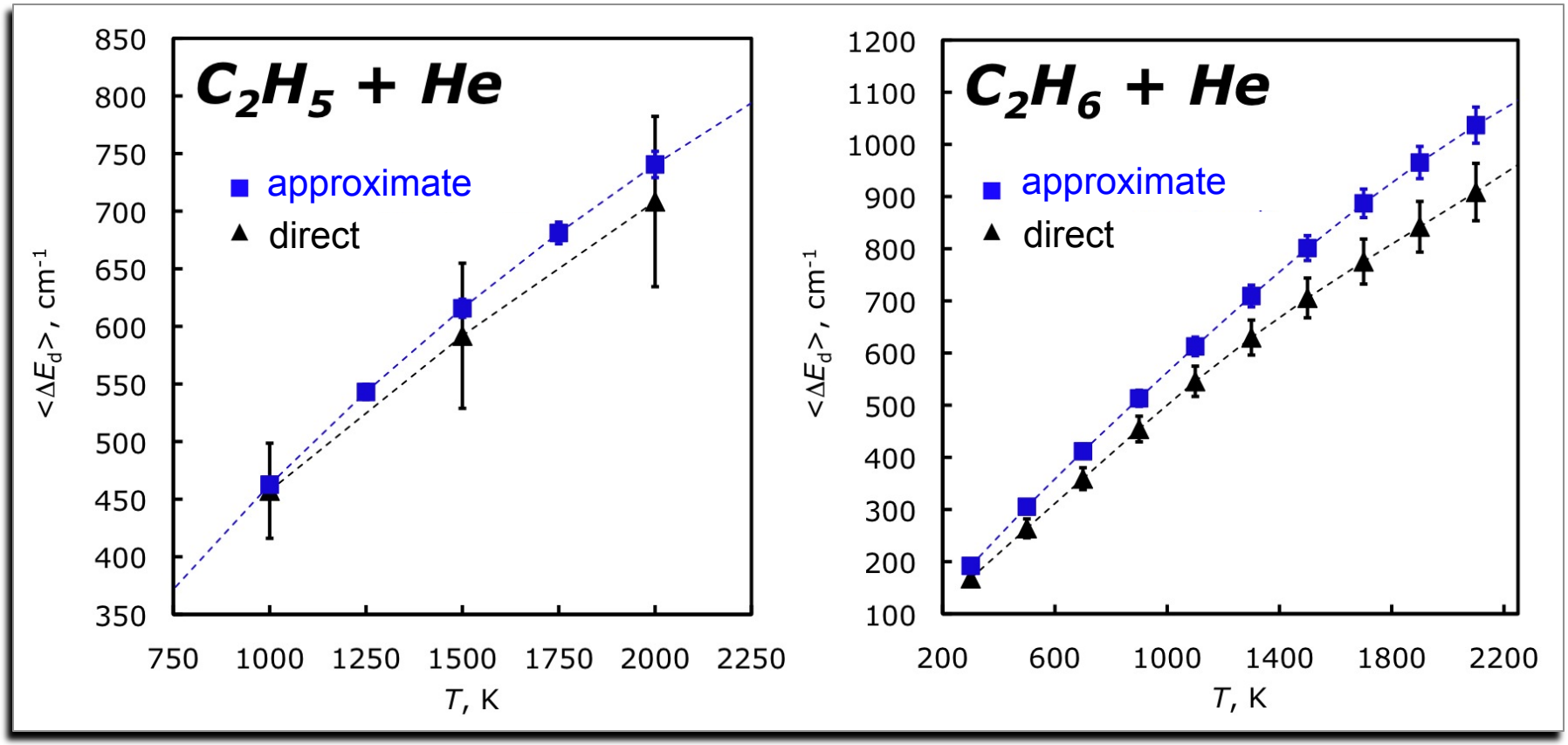
We tested our new parameter-free pressure-dependent kinetics against low pressure & falloff measurements





Direct dynamics is very accurate but can be expensive…

Test of new "universal" hydrocarbon forces for collisional energy transfer trajectories



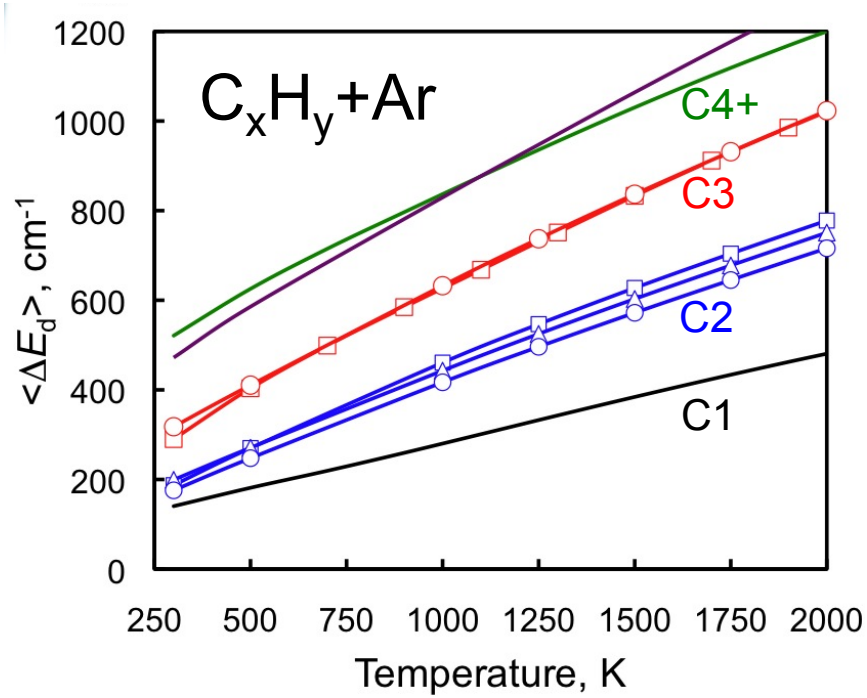
✓Direct dynamics: 6 CPU years

✓New force field: 6 CPU minutes

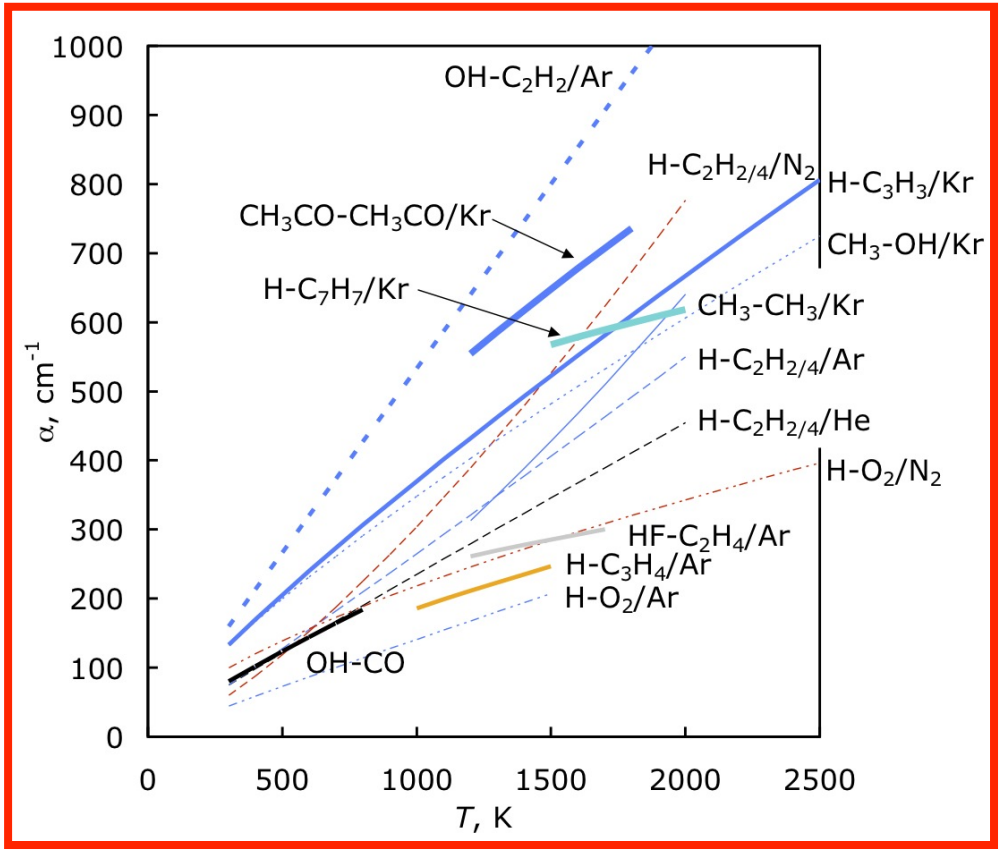
Speedup even better for larger systems!

Clear trends with respect to the target species

Calculated



Empirical

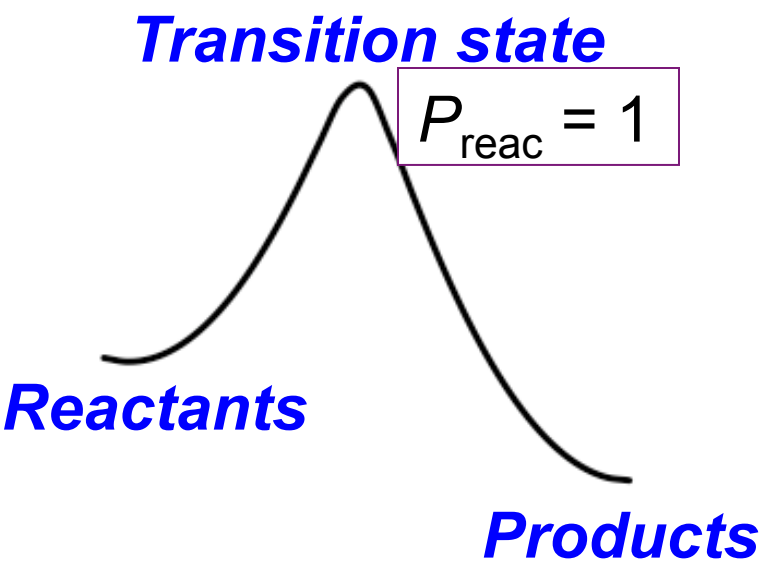


Challenge #3: Multistate kinetics

Example

^3O + singlet → singlet

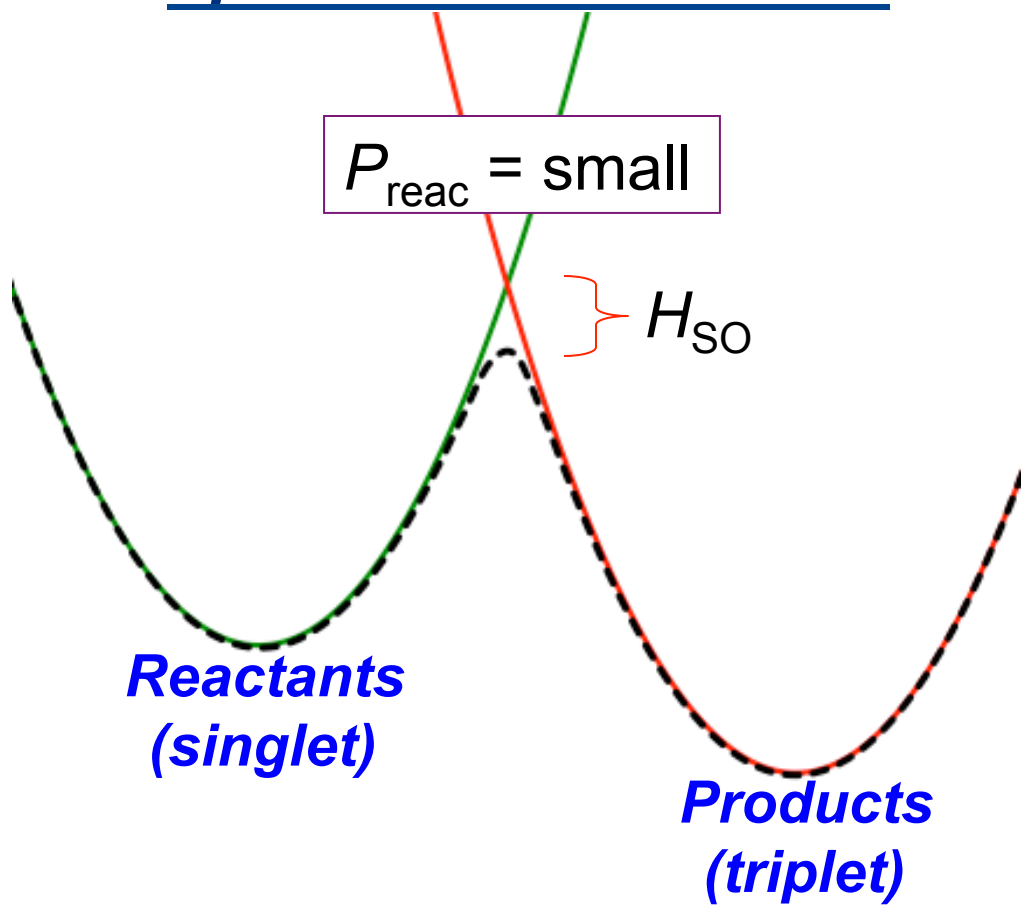
Adiabatic reaction



?

≈

Spin-forbidden reaction



Conclusions

Now: Predictive theoretical kinetics is possible

In favorable cases, rates can be predicted to "kinetic" (factor of 2) accuracy

Future: Three challenges to beating kinetic accuracy

1. Improved treatments of vibrational anharmonicity

Initial work underway: HPC critical to success

2. Validated models for collisional energy transfer

Quantitative trajectory based predictions using direct dynamics & HPC

A universal hydrocarbon force field was developed, applied to study trends

More validation studies underway for larger systems, radicals

We need simple rules for modelers

3. Validated models for spin-forbidden kinetics

We are studying the physics of spin-forbidden events to develop better statistical models

Future

CRF/Argonne approach

Single-reaction kinetics

experiments anchor theory

theory extrapolates beyond exp T & P

Detailed chemical mechanisms

experimental vs modeled

flame structures

autoignition
NOx
benzene/soot

Jasper: 50 k's in 6 years
Need: thousands

? *mechanism reduction*

Not done at the CRF

Less detailed mechanisms: reacting flows, soot, etc.

No feedback!

real engines, PreSICE

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~~Detailed chemical mechanisms~~

~~*experimental vs modeled*~~

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CRF initiative

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Feedback!

real engines, PreSICE

END