

Computer-Aided Construction of Chemical Kinetic Models: Towards *Predictive* Chemistry

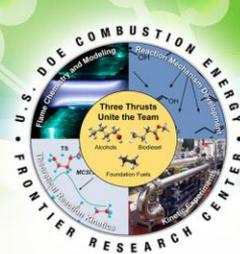
William H. Green

MIT Dept. of Chemical Engineering

DOE Combustion Meeting

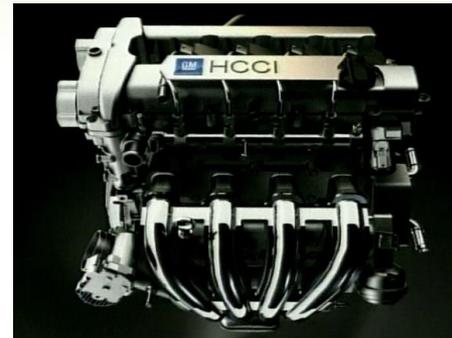
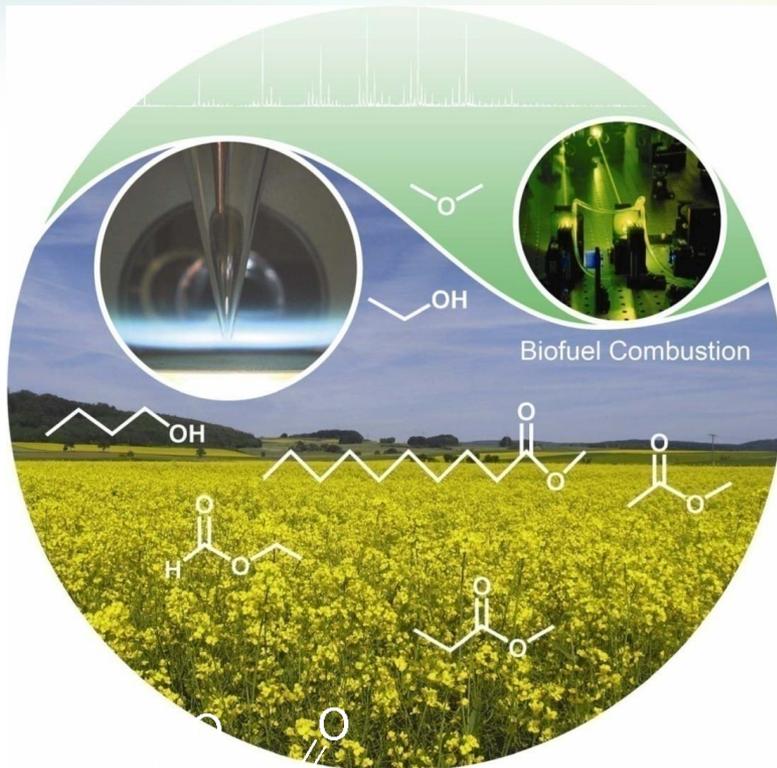
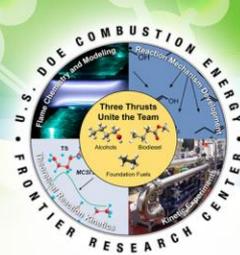
Potomac, MD, May 2014

Why do we want *predictive* fuel chemistry models?



- Historically, Fuels have changed pretty slowly... Engines evolved faster, using more-or-less static fuels. Fuel was a constant, not a variable...
- But now, fuels are changing!
 - To reduce greenhouse gas, laws require renewable fuels
 - Conventional light sweet petroleum is getting more & more expensive
 - Possible to make many future fuels with synthetic biology & chemistry
- **If fuel is a variable, we need to be able to predict how engine+fuel system depends on fuel composition, not just on engine & operating conditions.**
 - Much faster to explore new concepts on computer than by building prototype engines and synthesizing hundreds of barrels of a new fuel for engine tests
- Scientifically, we don't really understand something until we can make quantitative predictions...and discrepancies between those predictions and experiments reveal opportunities to learn something new!

Challenge: Lots of alternative fuels to evaluate!

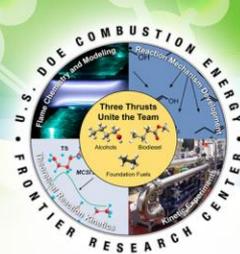


*And many
types
of engines,
too!*

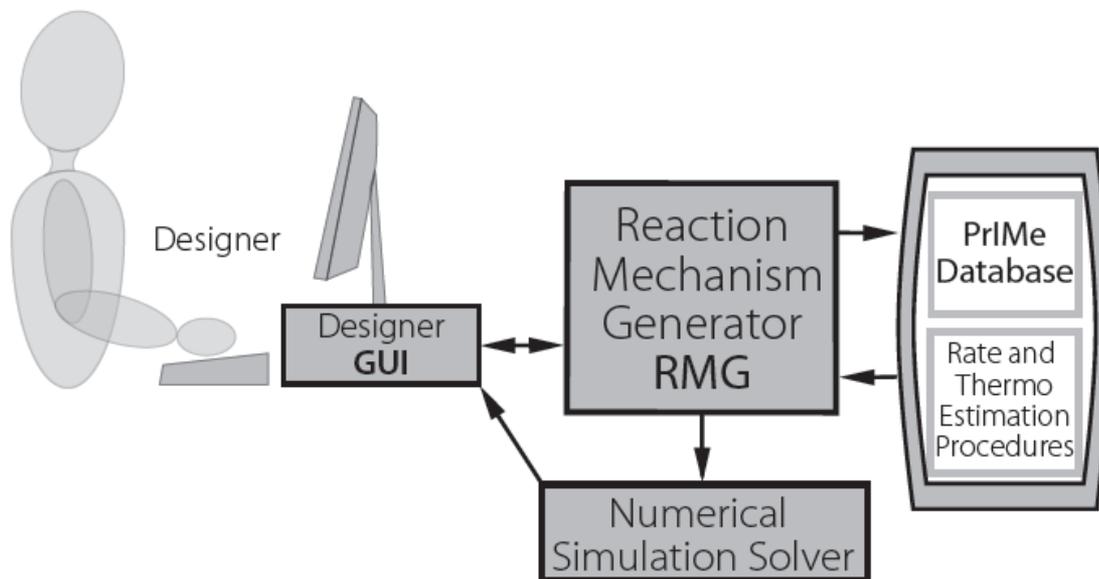
Not practical to synthesize & test every possible future fuel in every possible future engine...

...rapid, easy predictions are **valuable** and **needed**

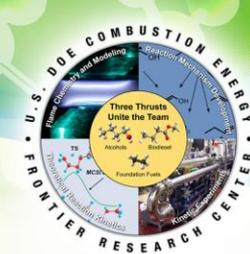
Automated Predictive Chemical Kinetics: The Concept & Motivation



- Rapid, Easy Predictions are *valuable & needed*
 - Assess alternative fuels & feedstocks
 - Design new processes and engines
- Hydrocarbon/Fuel chemistry is *complicated*
 - many reactions, species: need to automate

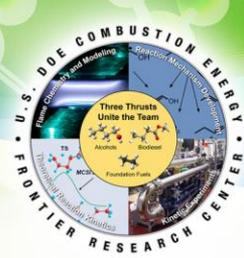


Fuel Chemistry models are *very* big!

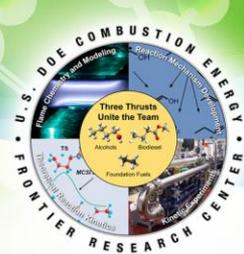


- Many chemical intermediates between fuel and CO₂.
- Multiple competing pathways
- Nonlinear, sometimes non-monotonic kinetics
- Real fuels (gasoline, jet, diesel) have many chemical species
 - So even initial conditions are complicated
- **Models built by hand: ~1,000 species, ~5,000 reactions**
 - Human tries to include just the more important reactions.
- **Models built by computer: ~500 species, ~10,000 reactions**
 - RMG software typically considers ~30,000 species and >100,000 reactions
 - most of them are found to be numerically negligible

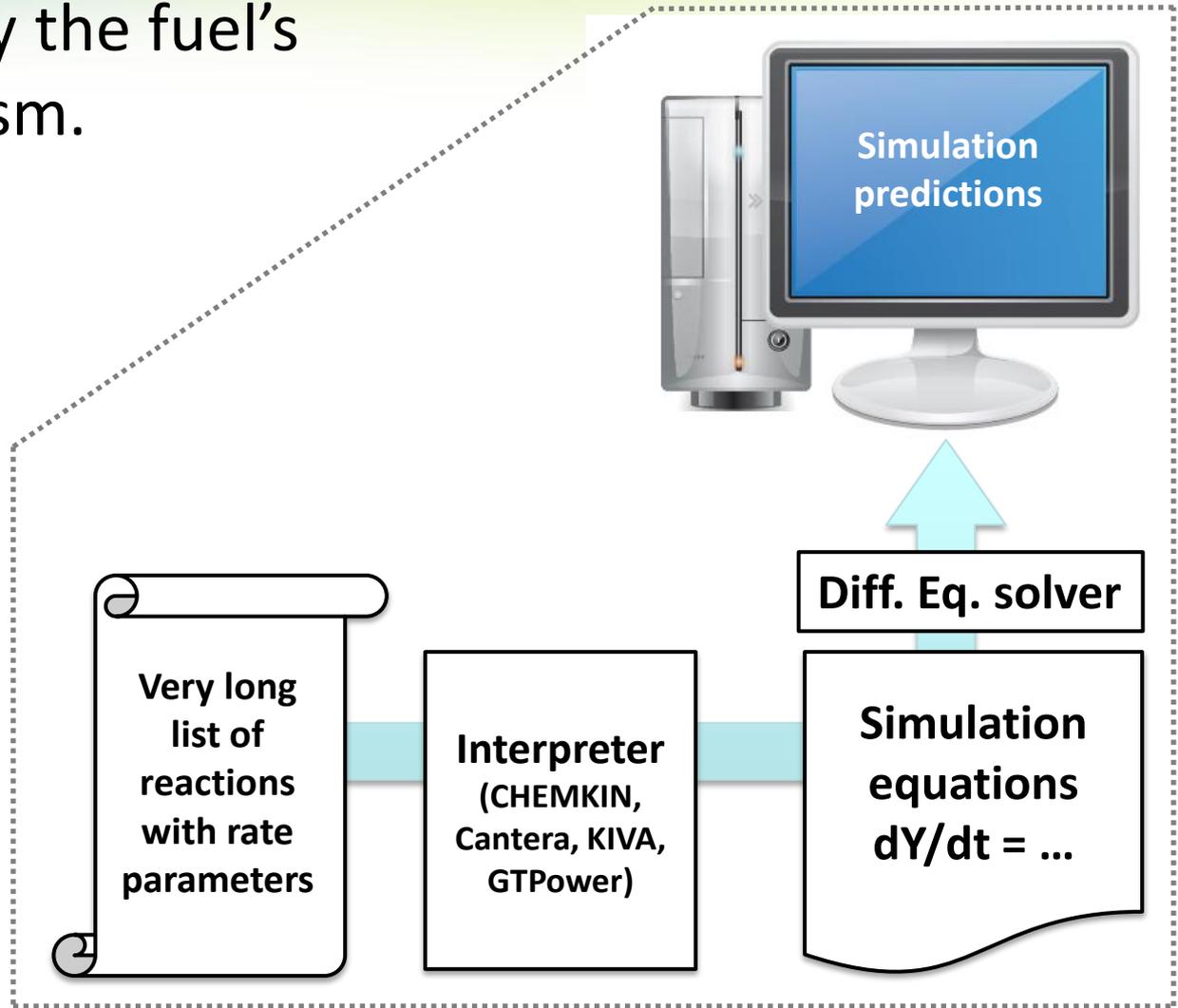
We need this black box



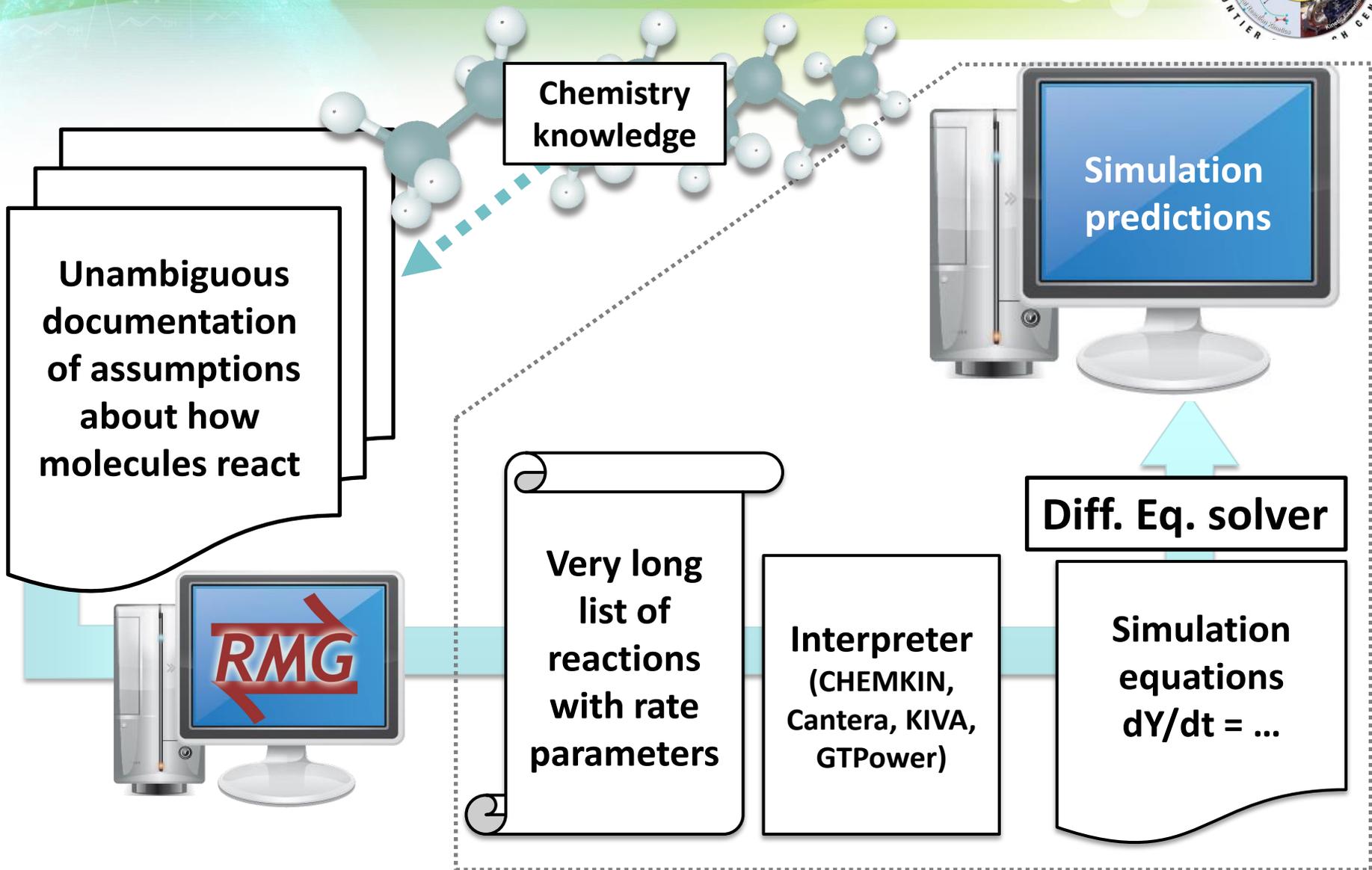
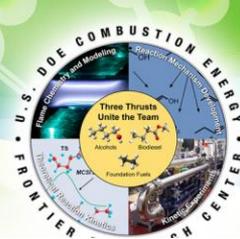
Similar issues for fuel-formation chemistry e.g. in refinery



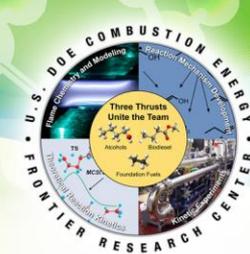
Commercial software can solve detailed kinetic simulations...
...*if* one can supply the fuel's reaction mechanism.



How we construct fuel chemistry models



Chemical Kinetic Modeling Challenges



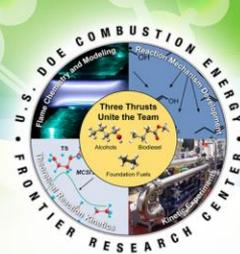
- **Identify all important reactions & species**
 - But not **unimportant** species & reactions: how to distinguish?
- **Estimate all reaction rate** coefficients (and properties, e.g. **thermochemistry**) to *sufficient* accuracy.
 - We use Functional Group extrapolations & **Quantum Chemistry**
- **Large models** pose numerical and computer problems
 - **Very challenging for humans** to handle, interpret, debug...
...SO WE TRY TO AUTOMATE EVERYTHING

We build on prior efforts by combustion research community, e.g.

Comprehensive Chemical Kinetics 35 (1997)

Advances in Chemical Engineering 32 (2007)

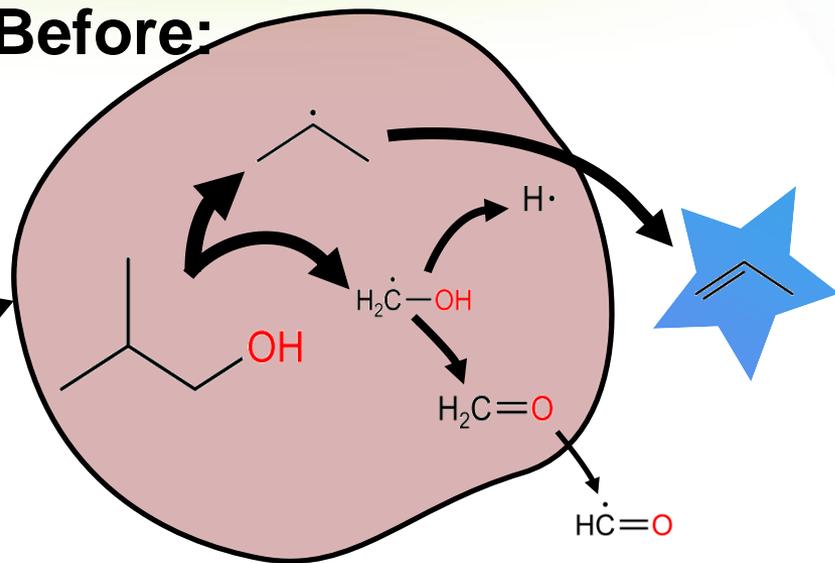
RMG algorithm: Faster pathways explored further, growing the model



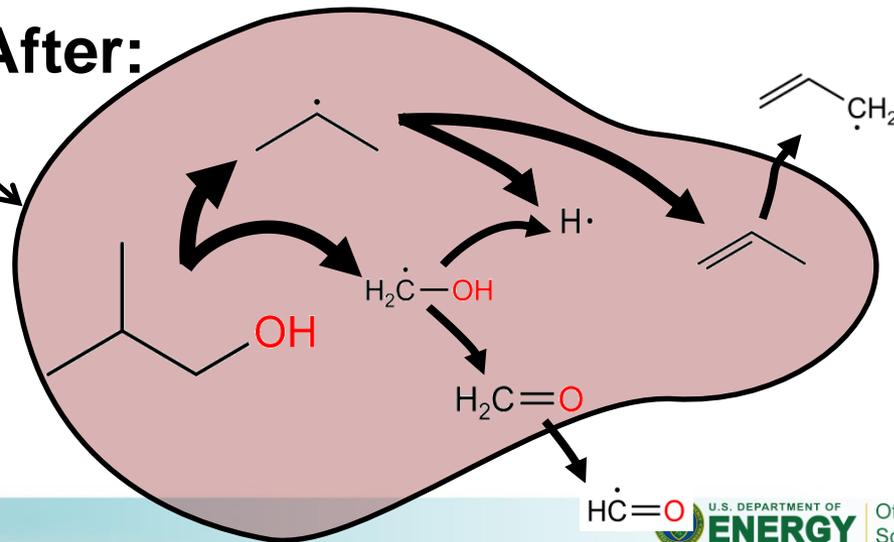
RMG

“Current Model” inside.
RMG decides whether
or not to add species to
this model.
Final model typically
~500 species, 8000 rxns

Before:

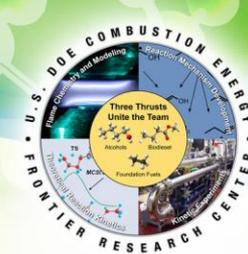


After:



*Open-Source RMG software.
Download from
rmg.sourceforge.net*

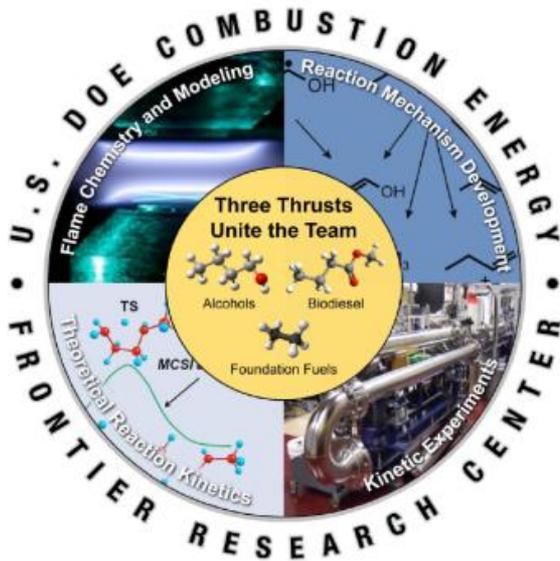
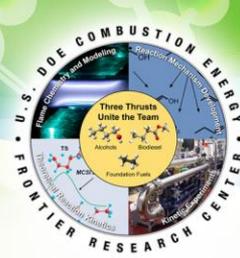
Kinetic Model Predictions Rely on Quantum Chemistry for Thermo, Rates



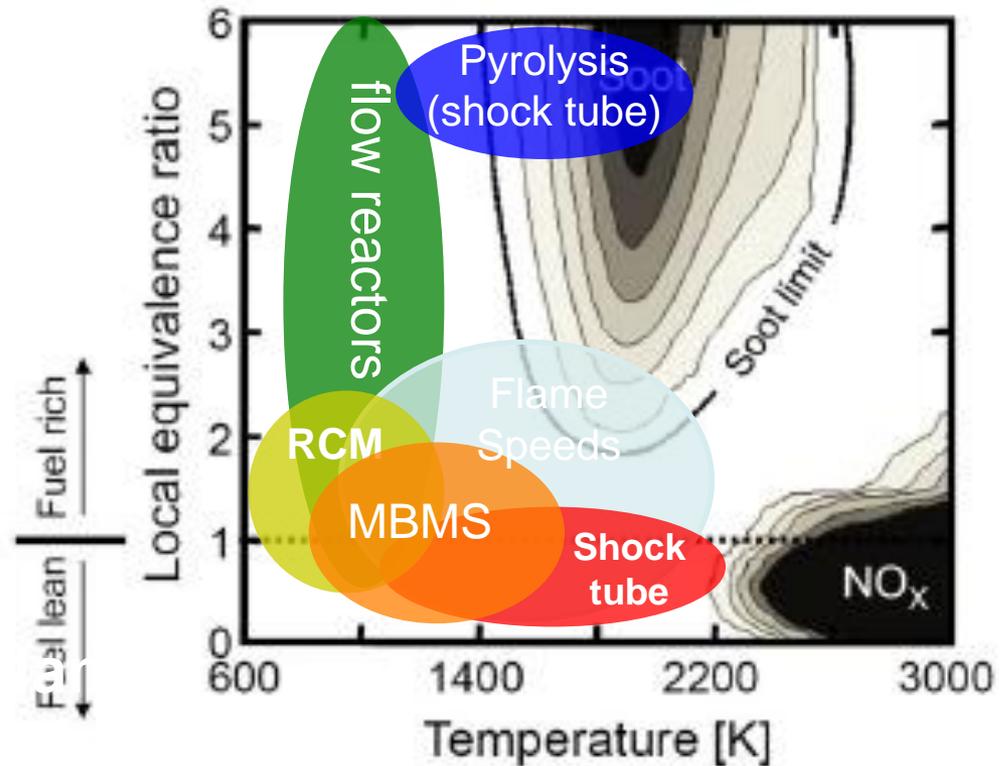
- Functional Group approximation
 - Compute a few examples of each reaction type with quantum, then use same barrier, A factor for analogous reactions.
- Most of our calculations at CBS-QB3 level
 - Geometries, Vibrational Frequencies from DFT
 - Single point energies at stationary points at higher level
 - Extrapolation to Basis Set Limit
- Recent calculations use F12 methods
 - Explicit dependence on distance between every pair of electrons
 - Much faster basis set convergence
- Most calculations rely on common approximations
 - Rigid-Rotor Harmonic-Oscillator approximation
 - Conventional Transition State Theory (dividing surface at saddle point)
 - Simple corrections for internal rotors and tunneling
 - Modified Strong Collision approx. for $k(T,P)$

Are computed thermo, rates accurate enough??

Testing Accuracy of Model Predictions vs. Experiment: CEFRC data on Butanols

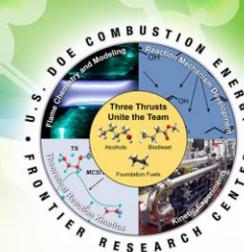


With collaborations from other institutes like Univ. Ghent, NIST.

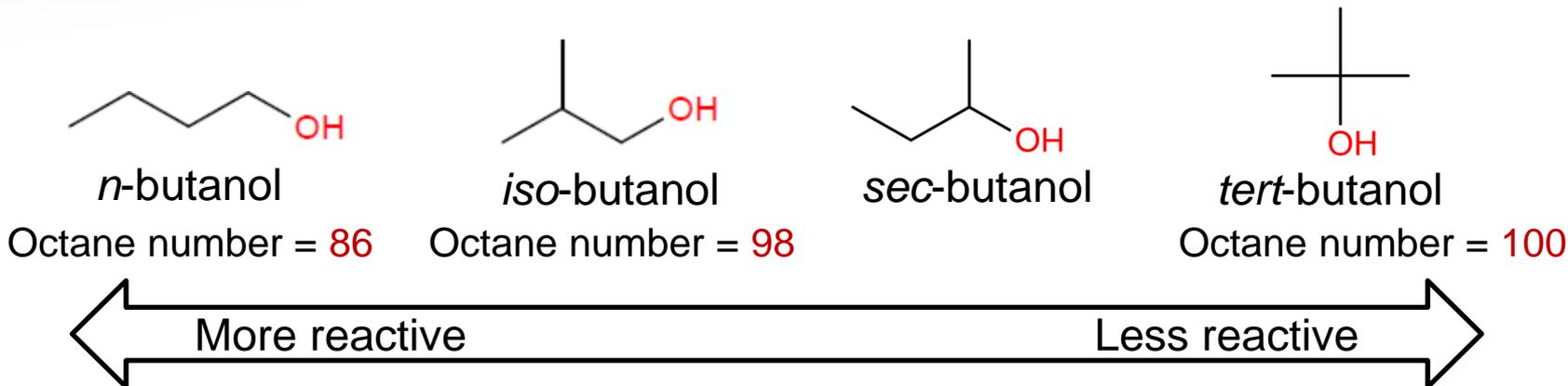


Rare Situation where detailed data available at many different conditions!

We used RMG to build a mechanism for butanol pyrolysis and combustion.



Four isomers, very different octane numbers.



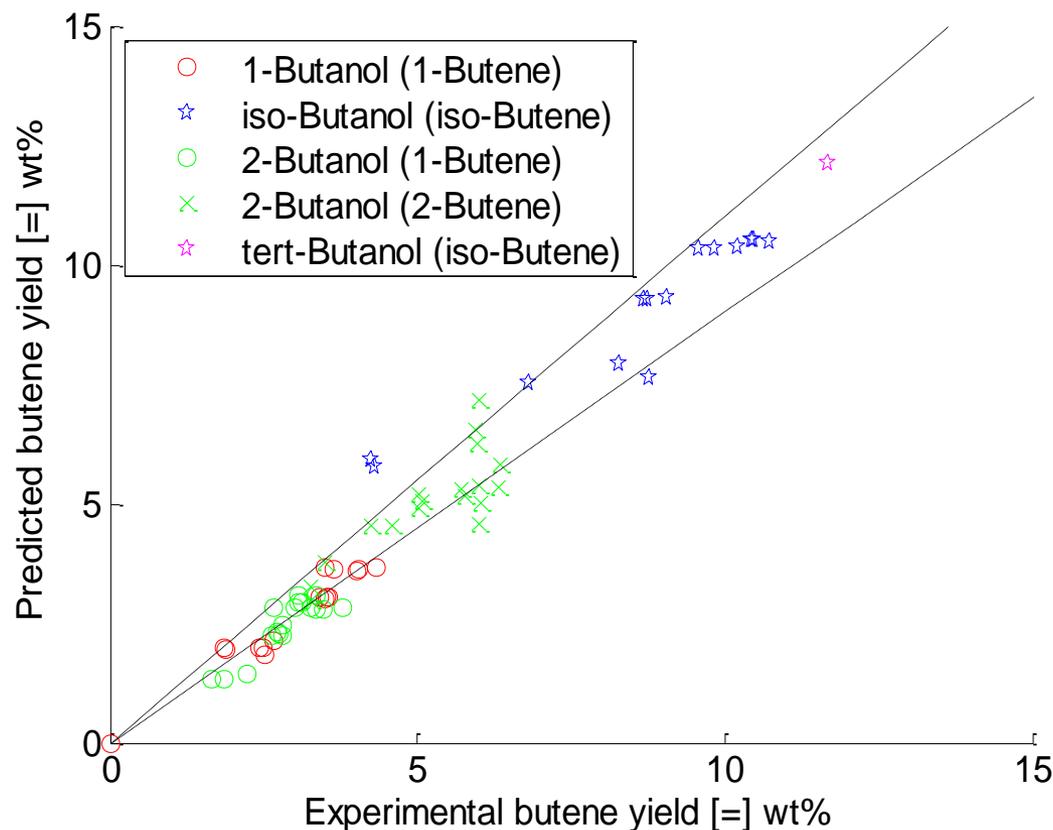
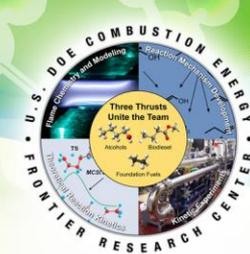
RMG considered about 30,000 possible species, selected as important:

- 372 chemical species
- 8,723 reactions



Important *k*'s with quantum chemistry

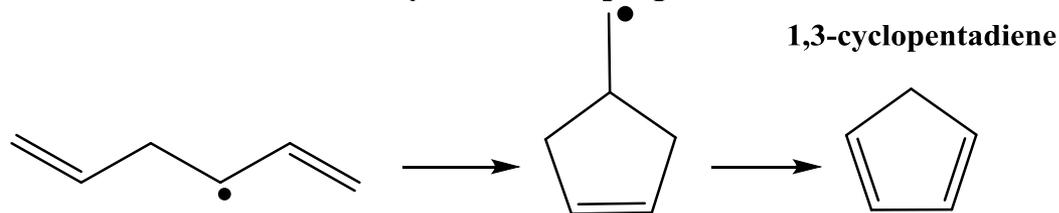
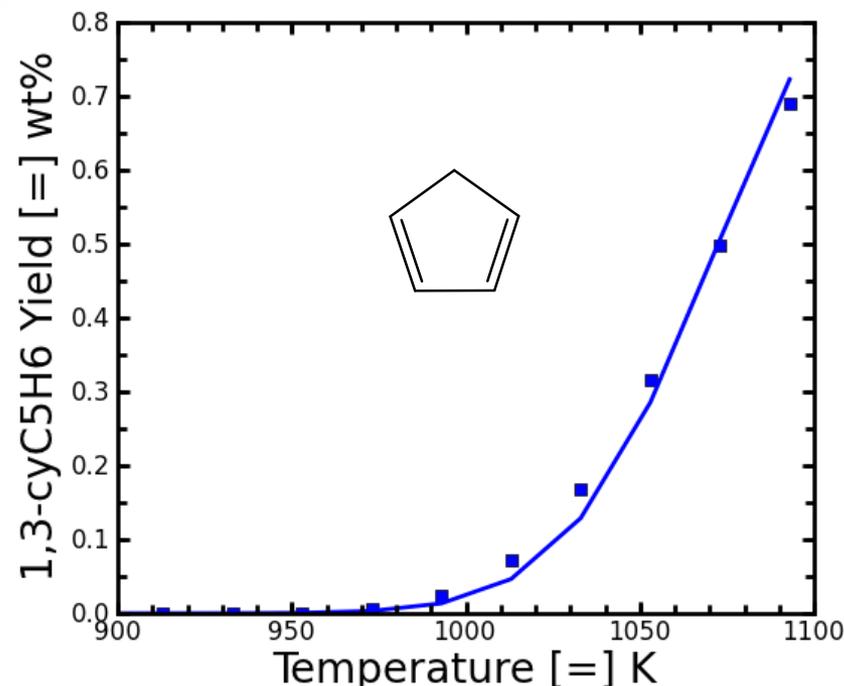
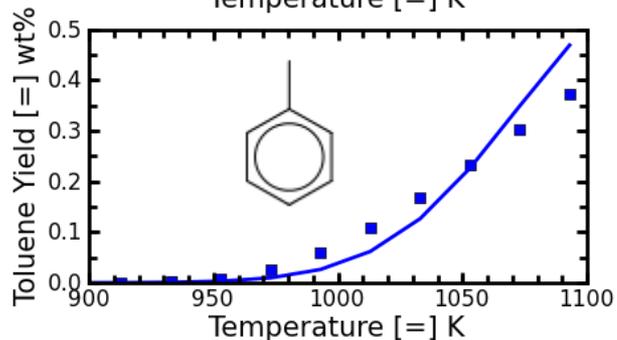
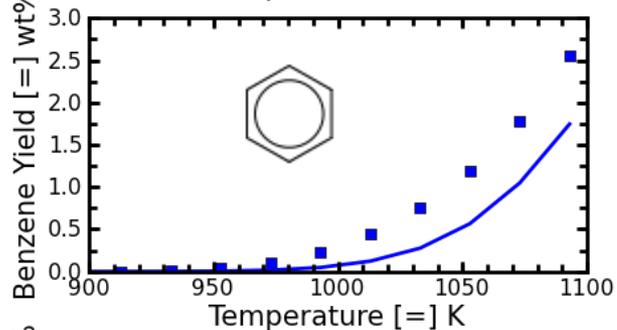
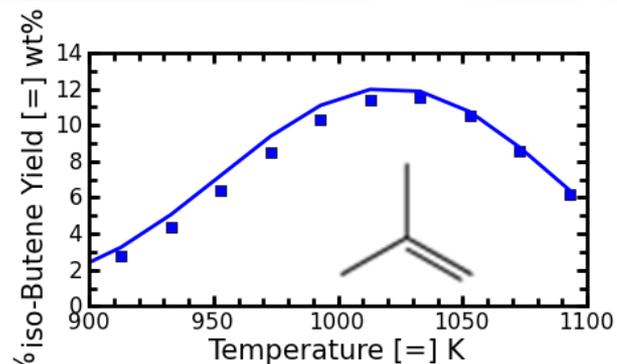
Model predicted butenes yield from butanols pyrolysis accurately



Pyrolysis,
T ~ 1000 K
P ~ 2 bar
t ~ seconds

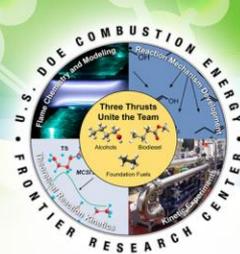
Experiments:
Van Geem et al.
Univ. Ghent

The kinetic model also quantitatively predicts formation of aromatics from butanols (via rather complicated reaction sequences)

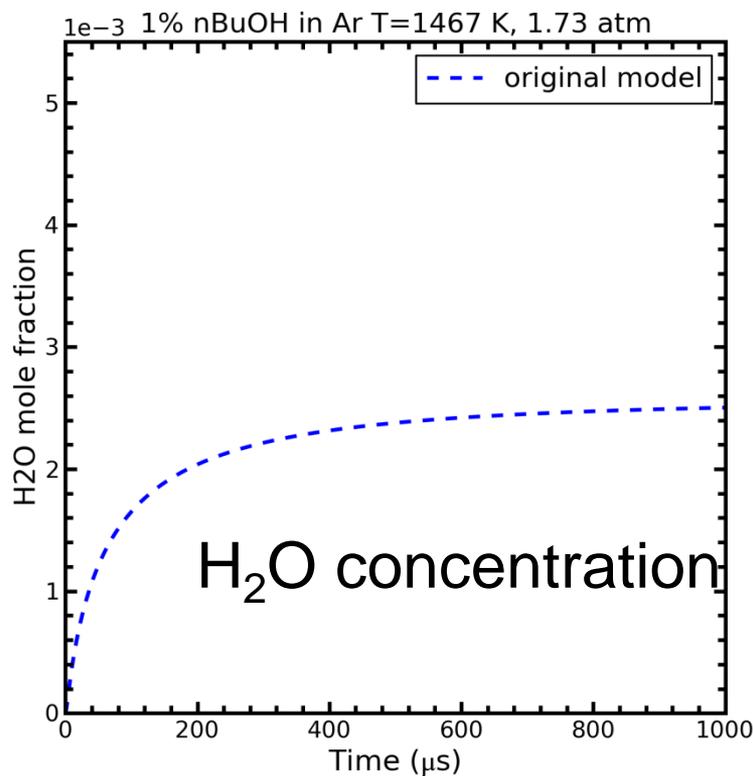
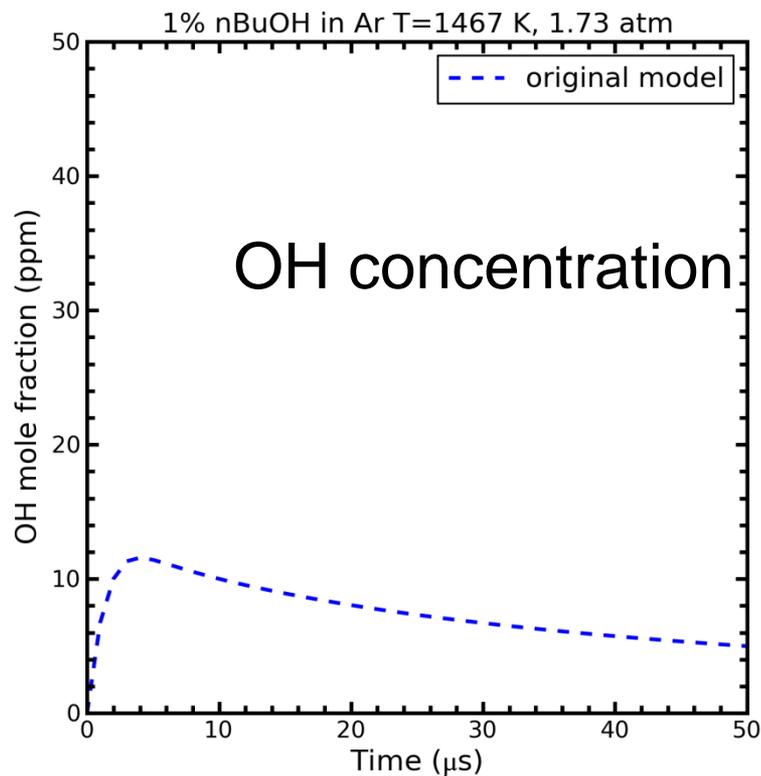


Data from K. Van Geem, Ghent
pyrolysis of *iso*-butanol ~1000 K, 2 atm, 2 seconds

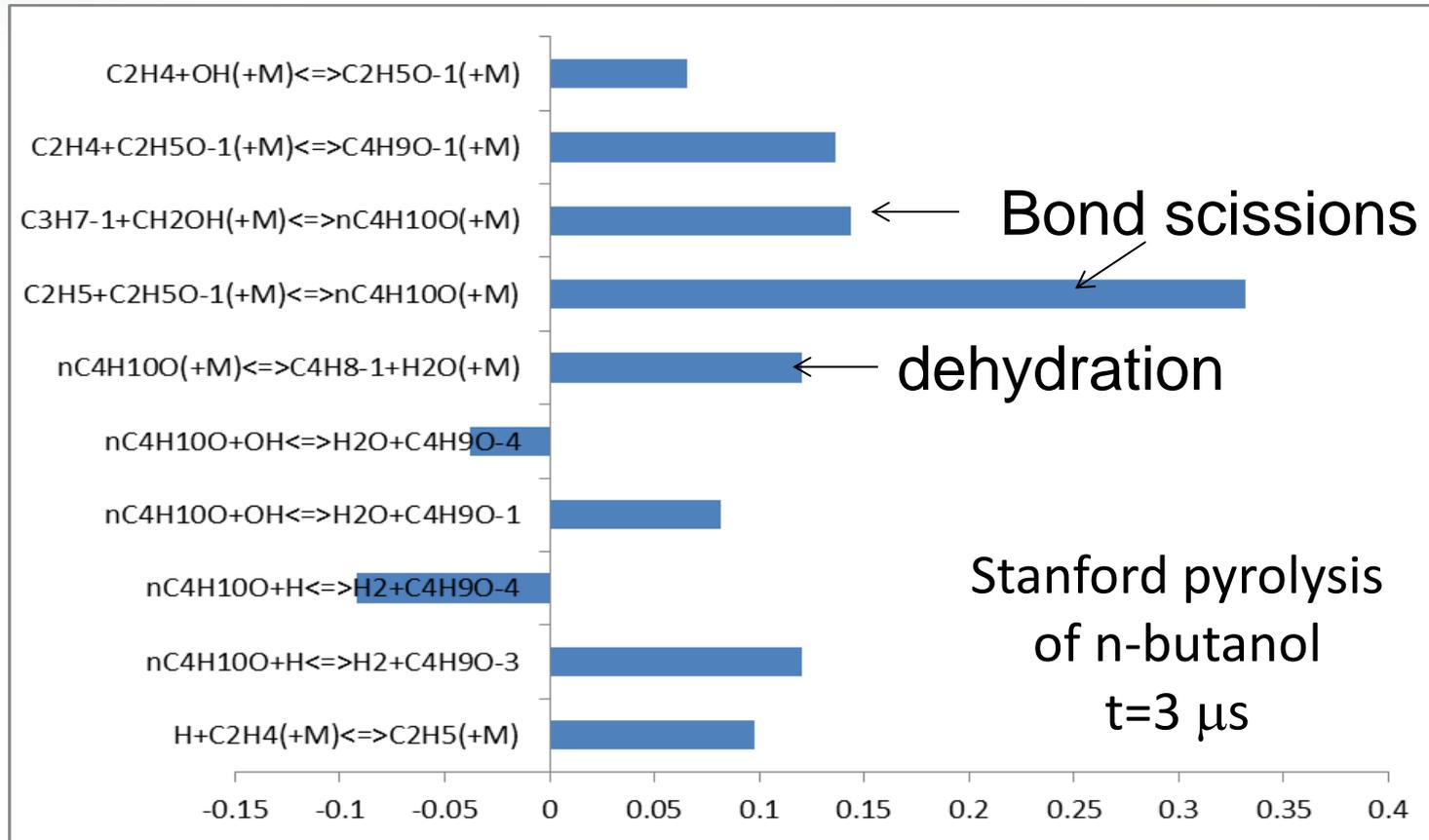
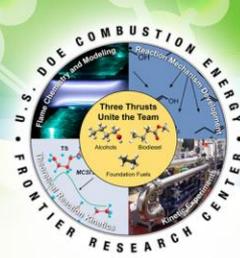
When you change reaction conditions, need to add reactions, compute rate coefficients



Predictions of 1000 K pyrolysis model for 1467 K

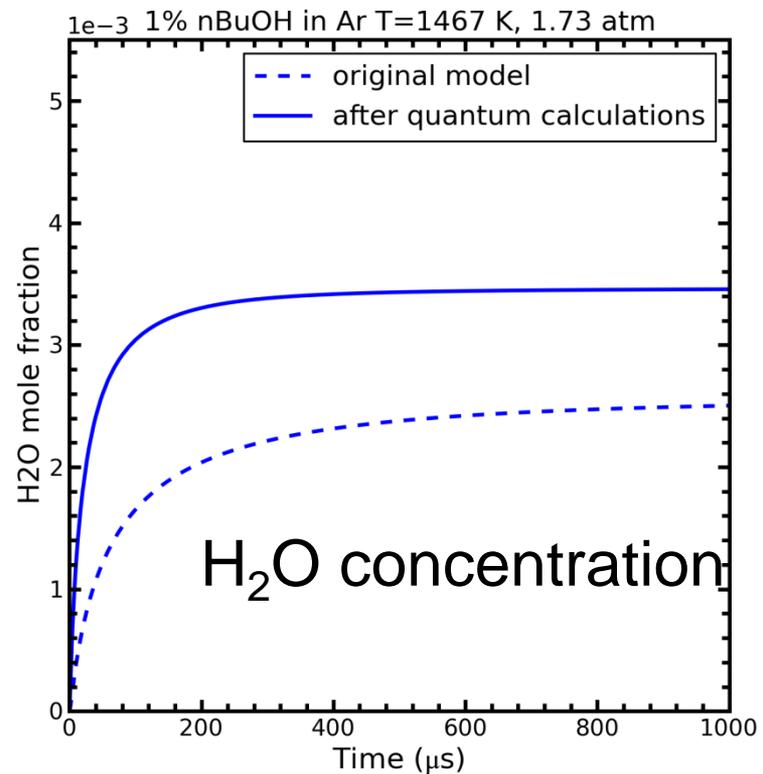
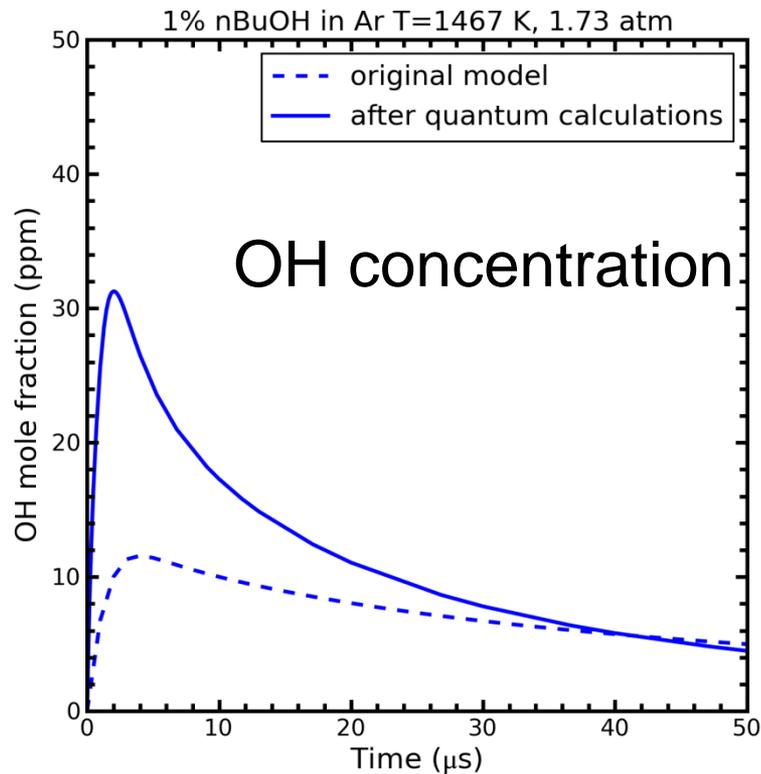
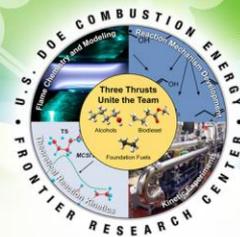


Microsecond H₂O formation at 1400 K sensitive to different reactions than long-time product formation at 1000 K.

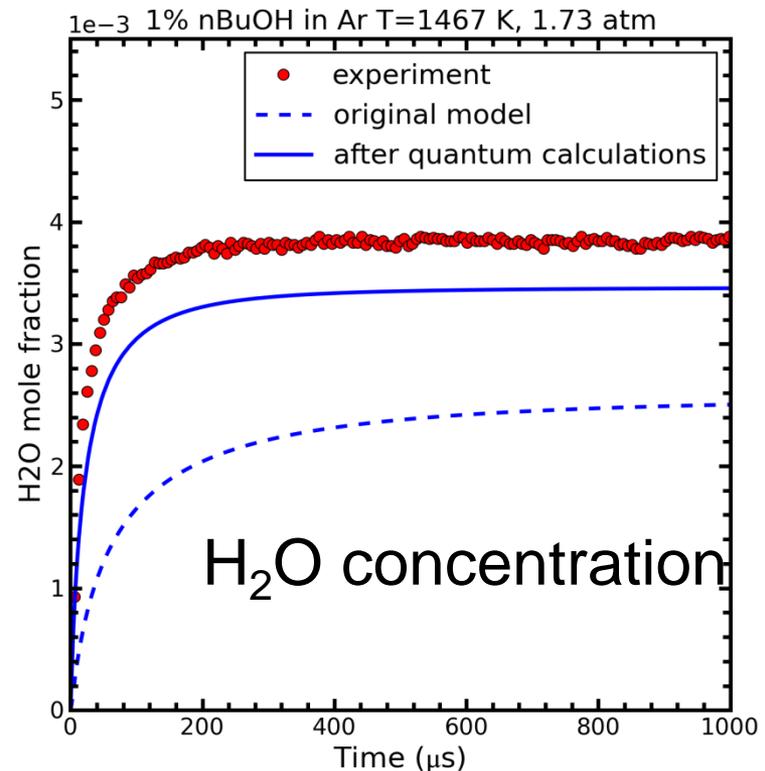
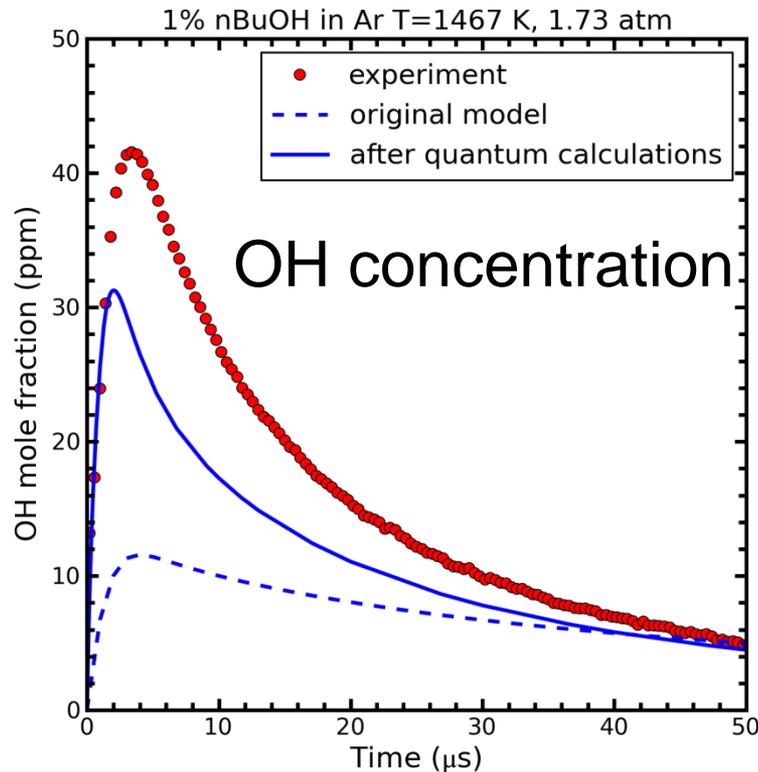
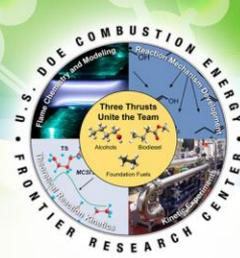


So... computed improved estimates of bond scissions & dehydrations based on quantum chemistry....

Quantum calcs for $k(T,P)$ sensitive at 1467 K significantly changes predictions



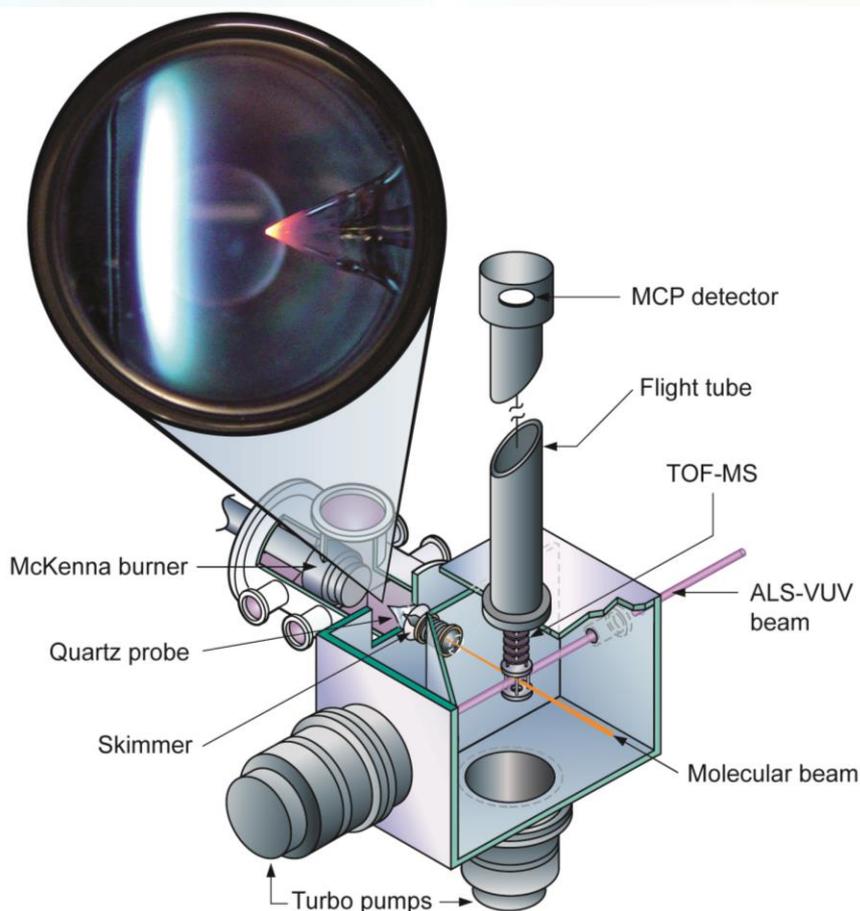
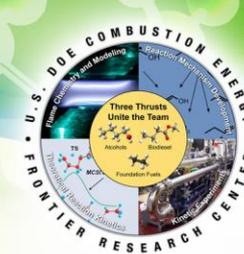
Using quantum calcs (rather than rough estimates by analogy) for most sensitive high T reaction $k(T,P)$ improves predictions of shock tube pyrolysis:
It is always a good idea to do the quantum calcs for the Sensitive numbers in the model!



Experimental data: Stranic et al., *Combust. Flame* (2012).

See also Rosado-Reyes et al., *J. Phys. Chem. A* (2013).

Advanced Light Source allows quantification of *dozens* of species including key radicals in flames



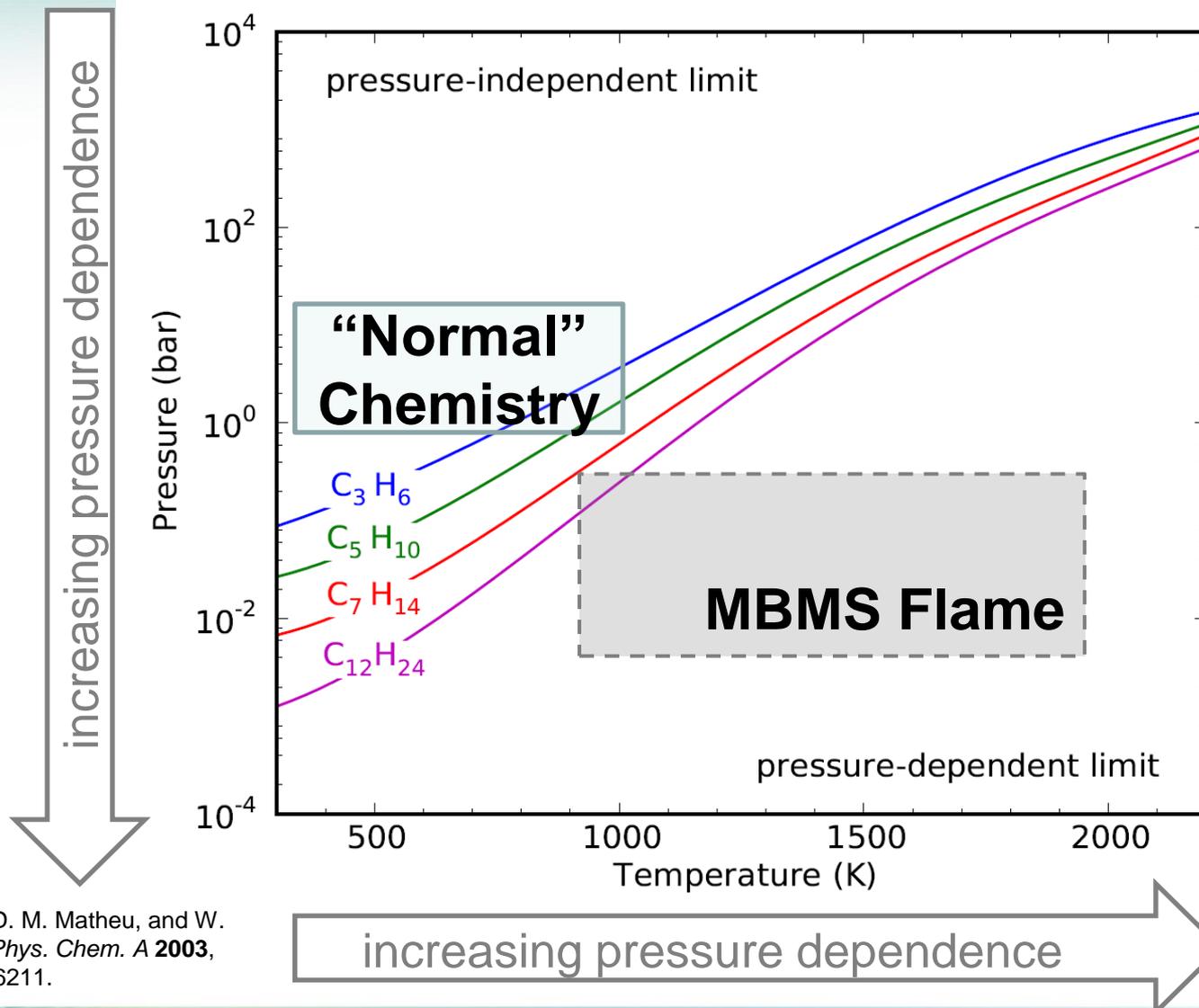
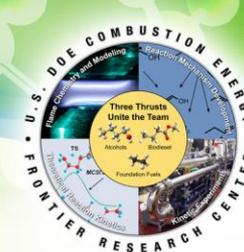
- Flames are analyzed with molecular beam time-of-flight mass spectrometry
- Photoionization with tunable synchrotron-generated VUV photons allows identification of species
 - by mass
 - by ionization energy

Data measured by Nils Hansen (Sandia) at Advanced Light Source (LBNL).

Hansen et al. PCCP (2012)

Hansen et al. Combust. Flame (2013)

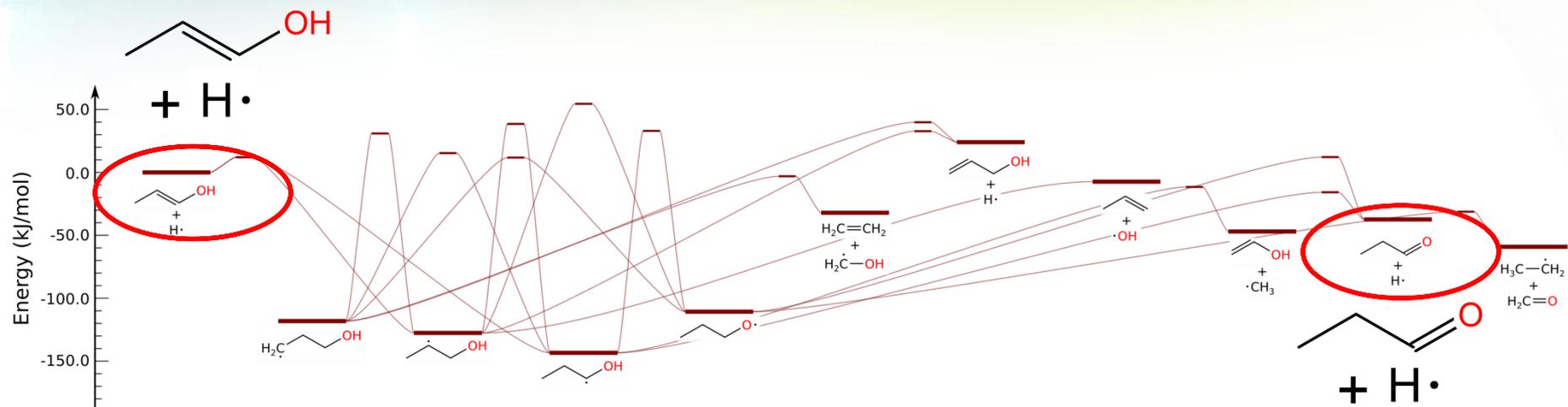
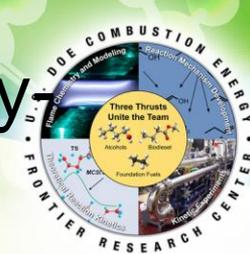
Often only a few small-molecule reactions are P-dependent. But in MBMS flames, *Many* Rates Strongly P-dependent



5,398
k(T,P)'s
in our
butanols
model...

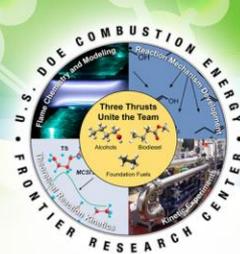
B. M. Wong, D. M. Matheu, and W. H. Green. *J. Phys. Chem. A* **2003**, 107, p. 6206-6211.

Enols sensitive to H-atom-catalyzed chemically activated keto-enol tautomerization

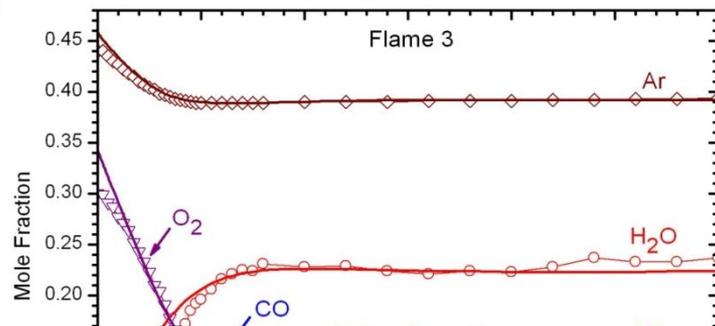
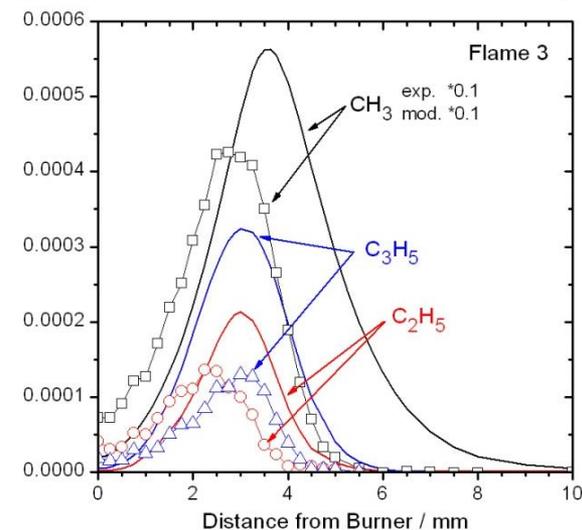
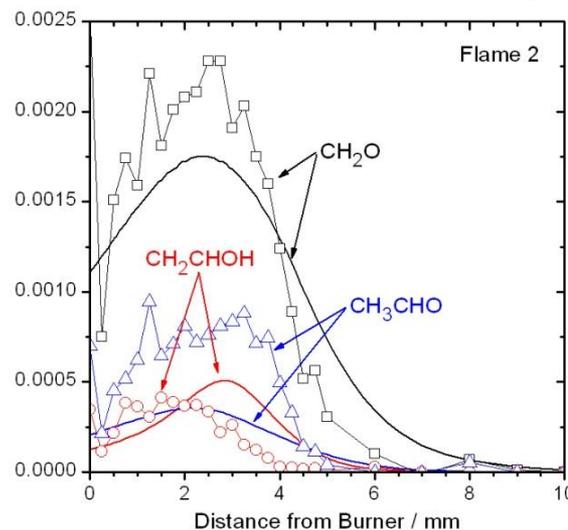
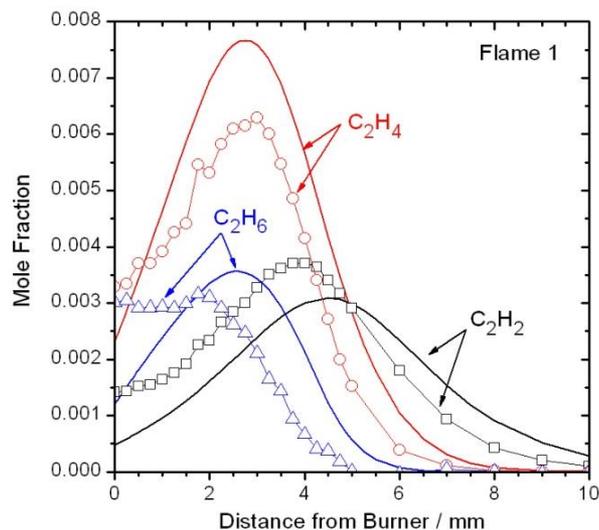


- ❑ “Chemically-activated” = “product reacts faster than thermalized”
- ❑ Chemical activation is a major complication in automated reaction generation: keep track of “well-skipping” reactions, compute $k(T,P)$
 - ❑ Instead of 2 possible products, 10 are formed.
 - ❑ Instead of 2 Transition States, must compute 16 TS’s.

Speciation profiles confirm predictive capabilities: n-butanol flame



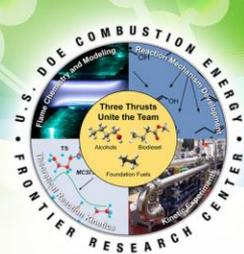
- Major species are predicted accurately
- A more powerful test is provided by comparing modeled and experimental profiles of intermediate species
- Originally one significant deviation, due to typo in thermo for one radical (C_4H_5)



Dozens of additional species traces, variety of flames: all show comparably good agreement.

For isobutanol we worked in predictive mode, with similar level of agreement with expt.

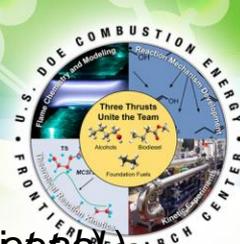
Significant uncertainties due to calibrations, uncertainties in $T(z)$, boundary conditions at burner, probe



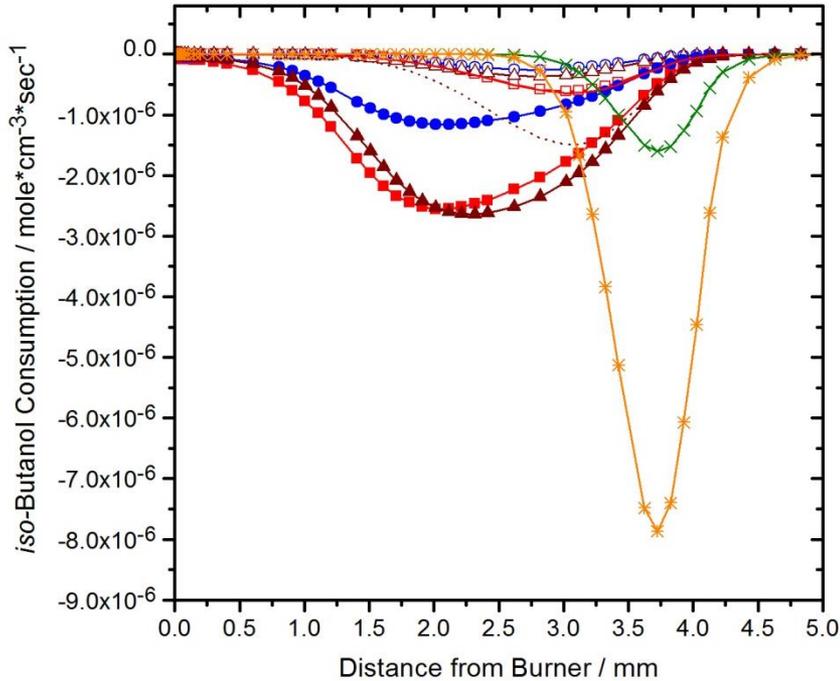
Our model *predicted* Hansen's MBMS measurements on isobutanol very well (see Hansen et al., Combust. Flame 2013)

However, Experimental Data consistent with a model prediction does NOT prove the model is correct!

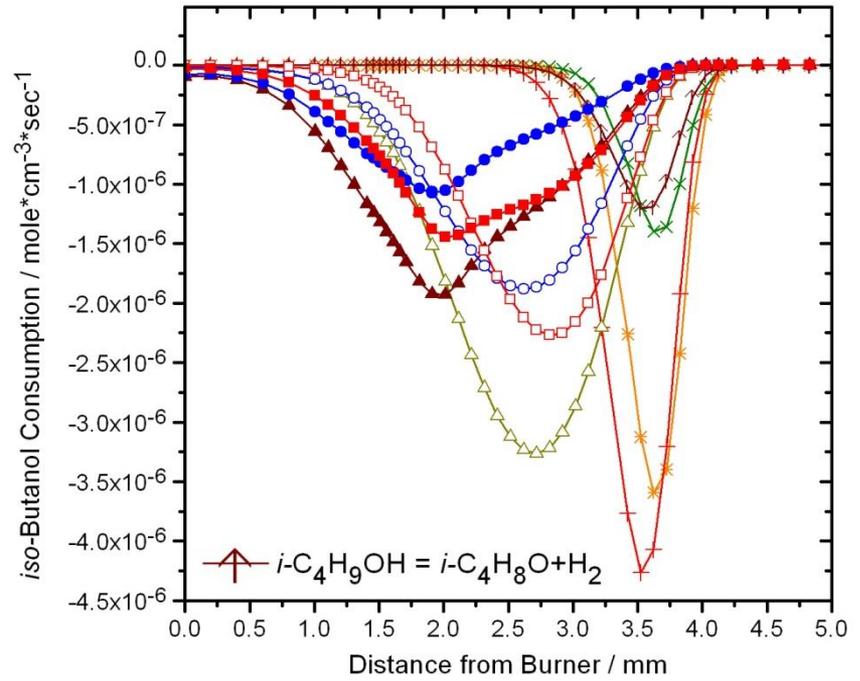
Although they all match MBMS data, Literature Models for *iso*-Butanol Flame Significantly Differ



MIT Model (Green group)



MIT Model (Sasulyte et al.)

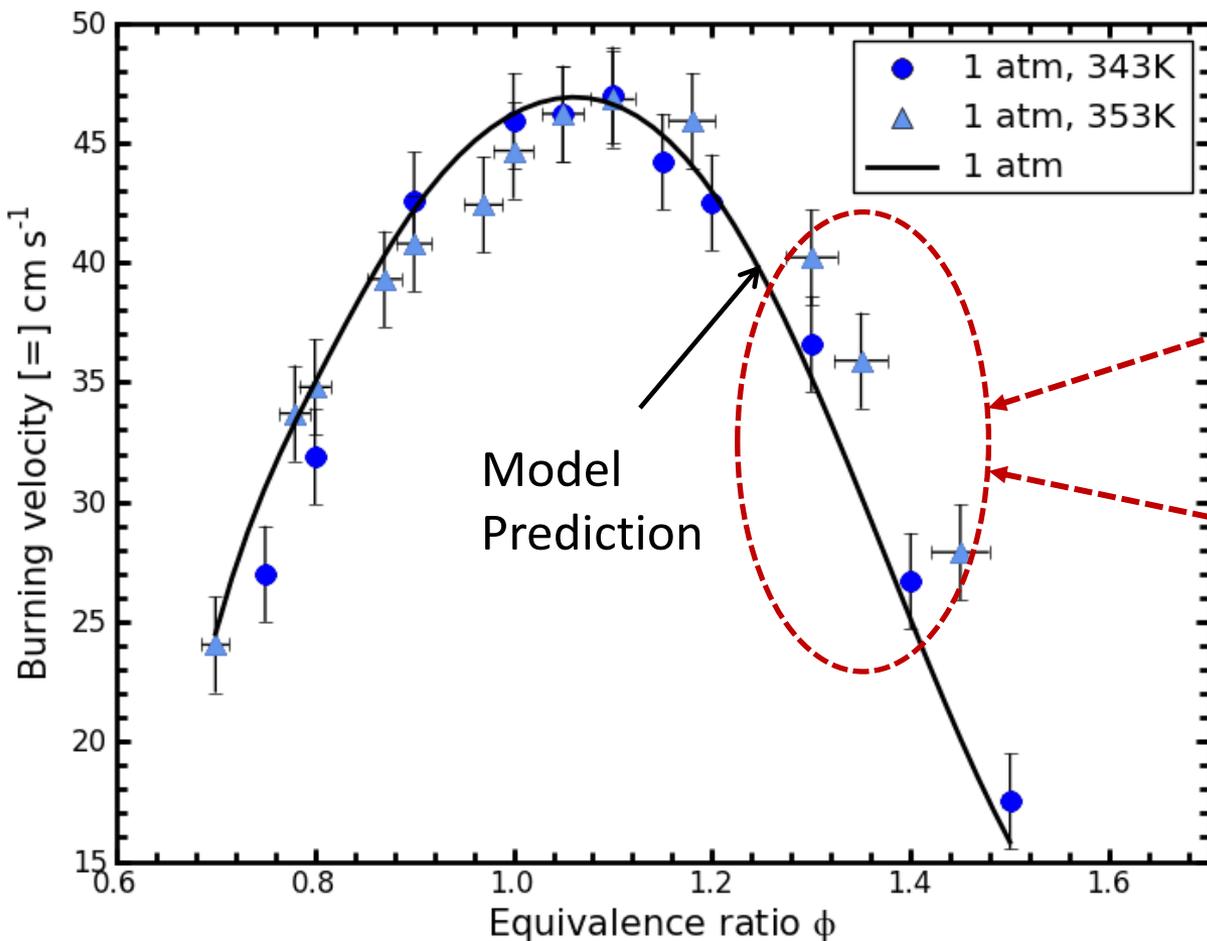
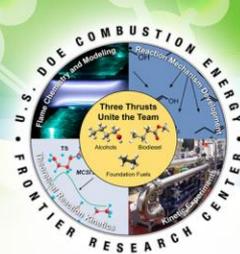


- $i\text{-C}_4\text{H}_9\text{OH} + \text{H} = \gamma\text{-C}_4\text{H}_9\text{O} + \text{H}_2$
- $i\text{-C}_4\text{H}_9\text{OH} + \text{OH} = \gamma\text{-C}_4\text{H}_9\text{O} + \text{H}_2\text{O}$
- $i\text{-C}_4\text{H}_9\text{OH} + \text{H} = \beta\text{-C}_4\text{H}_9\text{O} + \text{H}_2$
- $i\text{-C}_4\text{H}_9\text{OH} + \text{OH} = \beta\text{-C}_4\text{H}_9\text{O} + \text{H}_2\text{O}$
- △— $i\text{-C}_4\text{H}_9\text{OH} + \text{H} = \alpha\text{-C}_4\text{H}_9\text{O} + \text{H}_2$
- ▲— $i\text{-C}_4\text{H}_9\text{OH} + \text{OH} = \alpha\text{-C}_4\text{H}_9\text{O} + \text{H}_2\text{O}$
- ▽— $i\text{-C}_4\text{H}_9\text{OH} + \text{H} = \omega\text{-C}_4\text{H}_9\text{O} + \text{H}_2$
- $i\text{-C}_4\text{H}_9\text{OH} + \text{O} = \gamma\text{-C}_4\text{H}_9\text{O} + \text{OH}$
- ×— $i\text{-C}_4\text{H}_9\text{OH} (+\text{M}) = \text{CH}_3 + \text{CH}_3\text{CHCH}_2\text{OH} (+\text{M})$
- +— $i\text{-C}_4\text{H}_9\text{OH} (+\text{M}) = i\text{-C}_4\text{H}_8 + \text{H}_2\text{O} (+\text{M})$
- - - $i\text{-C}_4\text{H}_9\text{OH} + \text{O} = \alpha\text{-C}_4\text{H}_9\text{O} + \text{OH}$

Many parameters in detailed kinetic models:
just because it matches experiment does not
mean it is the truth!

Slide from Nils Hansen

Flame Speed predictions look good – but are they accurate enough? What accuracy needed?

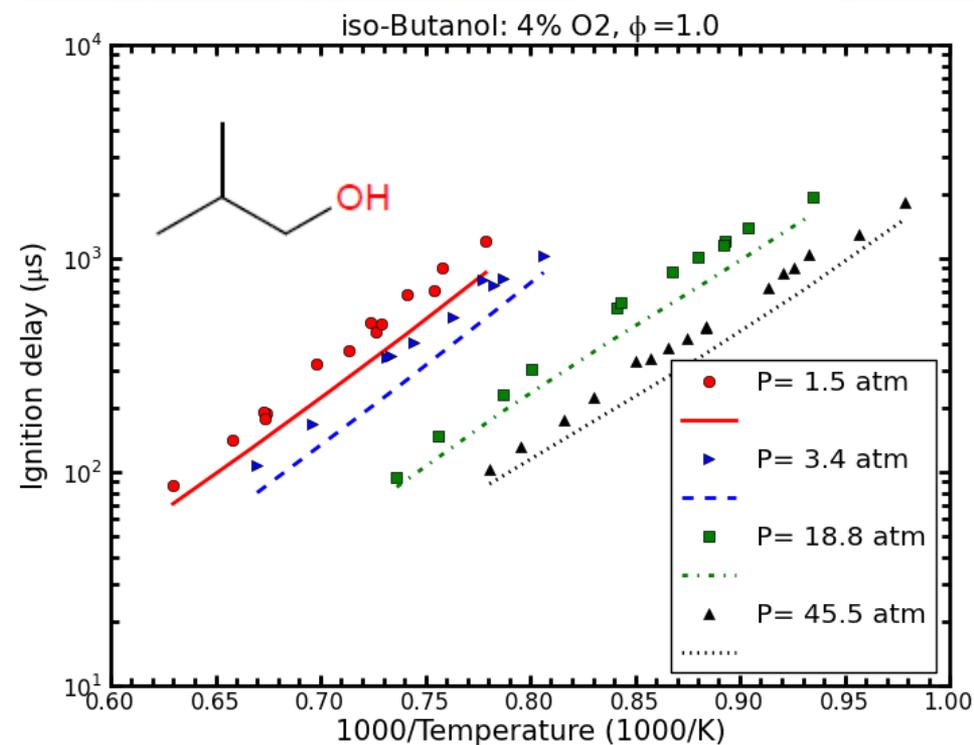
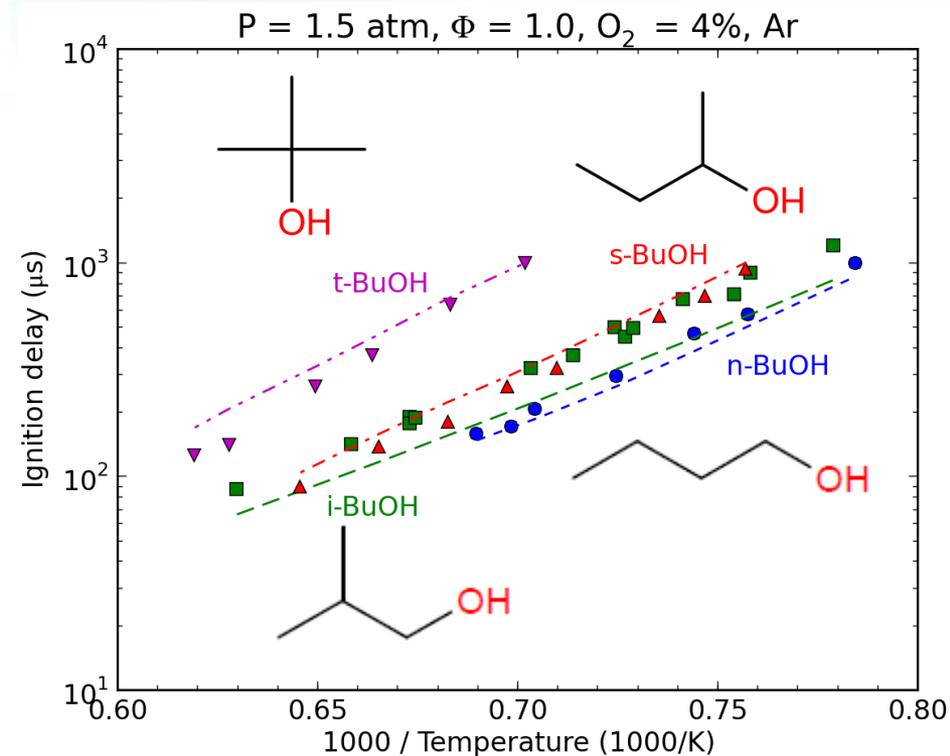
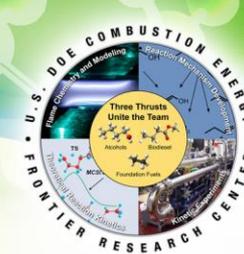


Experimentally-derived numbers not completely consistent, involve tricky extrapolation to zero strain. Error bars may be underestimated?

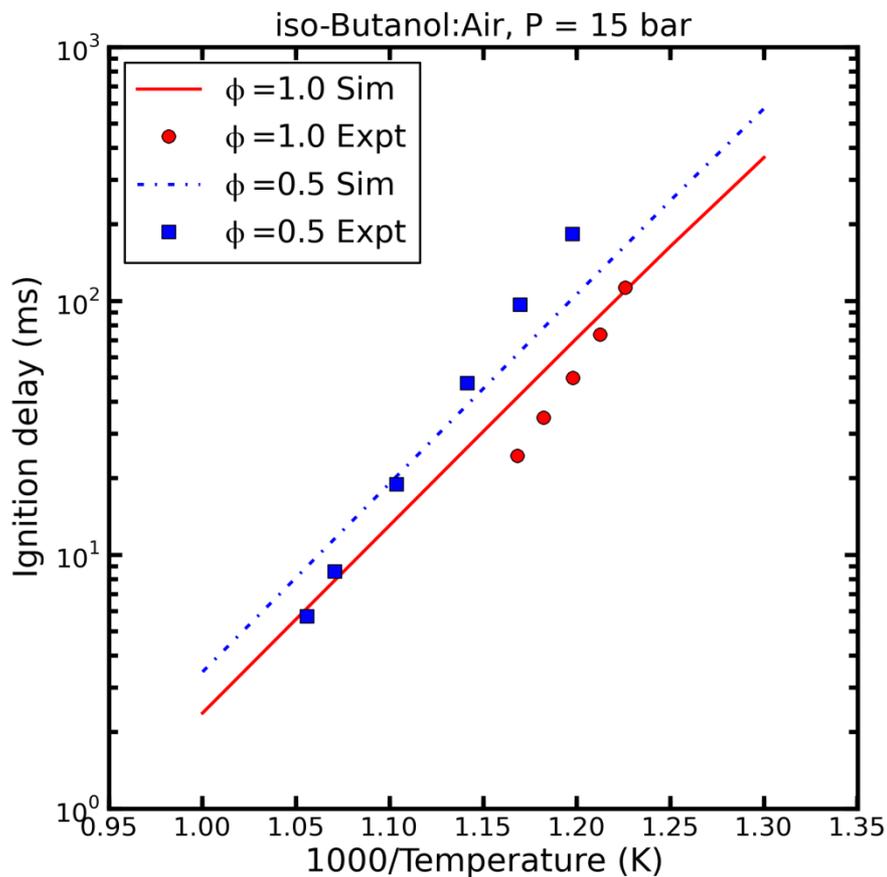
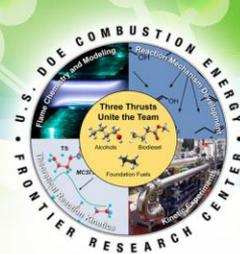
Model very sensitive to $\text{HCO} + \text{H}_2\text{O} = \text{H} + \text{CO} + \text{H}_2\text{O}$. This k alone leads to uncertainties in predicted flame speed comparable to deviations on this plot.

Data from Veloo & Egolfopoulos (343 K), and W. Liu ... & C.K. Law (353 K), both in Proc Combust Inst (2011).

Model quantitatively predicts high-T ignition delays for all butanol isomers & conditions



Model also predicts low-T ignition delays in air at conventional conditions fairly well, and the dependence of τ on [fuel]

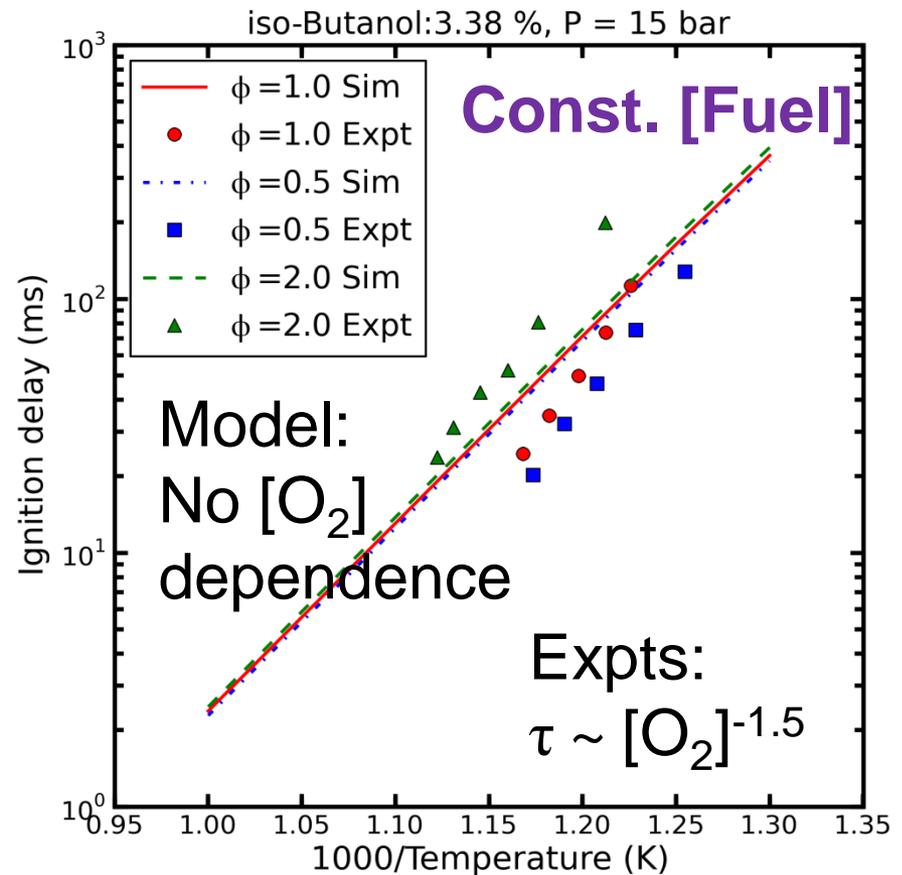
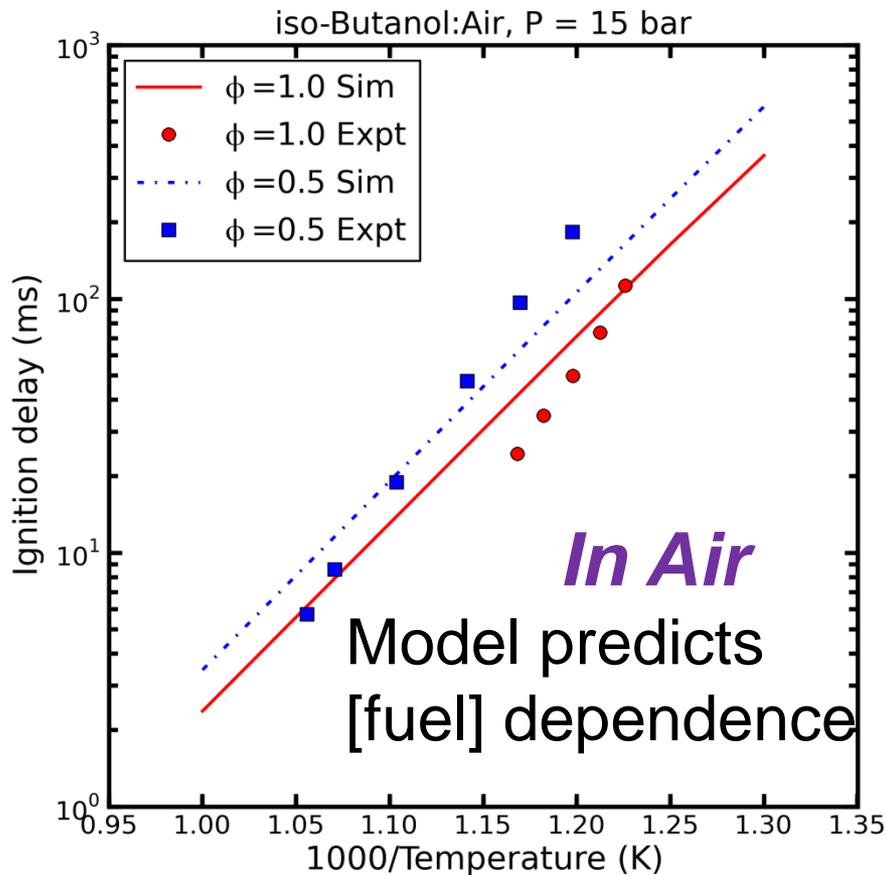
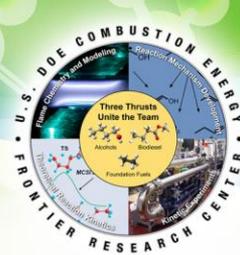


In these RCM experiments by Weber & CJ Sung, P & N₂:O₂ ratio is held fixed (as in air), and so [O₂] is also effectively fixed.

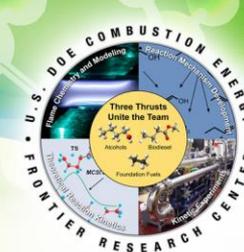
Most expts are done this way.

Then changes in ϕ are mostly changing [fuel].

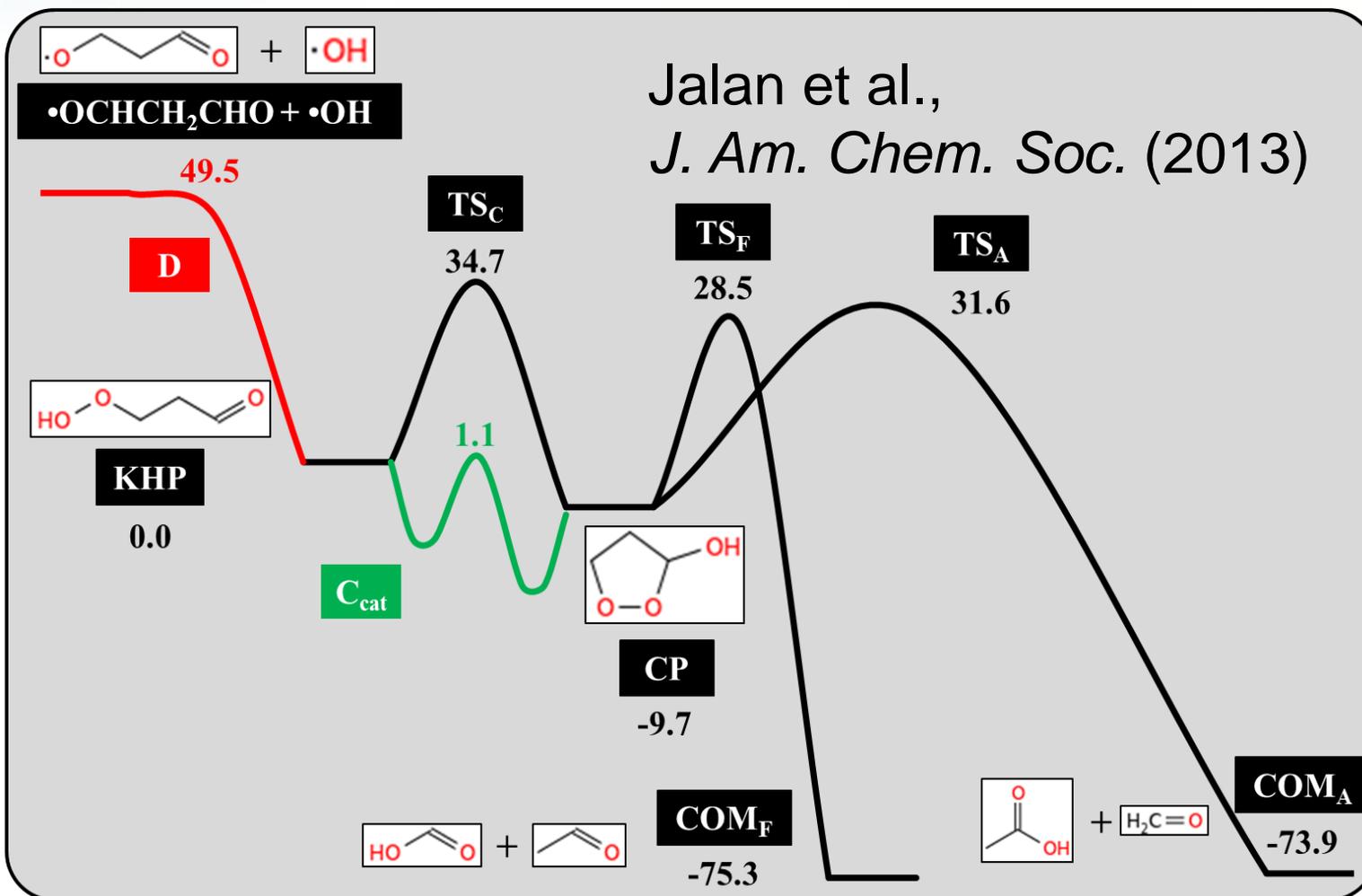
We don't know everything: model completely mis-predicts $[O_2]$ sensitivity of low-T ignition delay of butanols!



Discrepancy Led To Discovery of New Type of Reaction of Peroxides, Dominant at Low T, longer t (JSR or liquid phase)

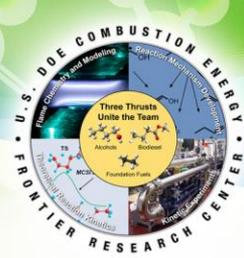


Jalan et al.,
J. Am. Chem. Soc. (2013)



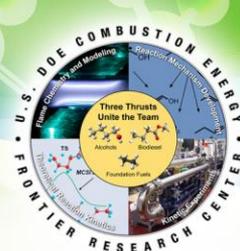
Green
& Truhlar
Groups

It's not just butanols...Green group recently made predictive models for many other fuels where fewer data are available

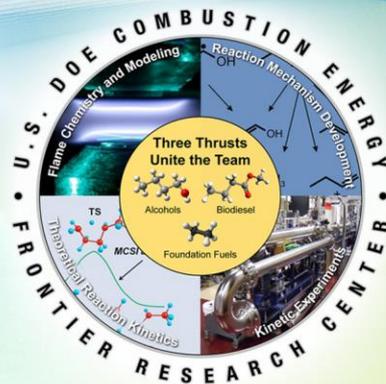


- **Di-isopropyl Ketone** (large collaboration with Sandia etc.)
 - See Allen et al., Combust. Flame (2014)
- **Ethylamine** (Buesser et al., about to be submitted)
- **JP-10** (in collaboration with Ghent, Aerodyne)
- Decane mixtures w/iso-octane & toluene (**surrogate jet fuel**)
- **Cineole** (in collaboration with Sandia)
- **Pentanol** (in collaboration with Xi'an, Ghent)
- **Iso-Pentanol** (in collaboration with Ghent)
- Thioethers & Thiols (**organosulfur**) pyrolysis
- **Phenyldodecane** pyrolysis

Summary



- Kinetic models based on quantum chemistry + rate estimates are **predictive** for huge range of combustion/oxidation/pyrolysis experiments.
 - **Big models can be built and refined pretty quickly.**
 - **Experimentalists + Theorists team very effective.**
 - Quick to identify and resolve discrepancies, whether due to model or expt.
 - **Method useful for assessing proposed new biofuels**
- We are working to extend method to more complicated fuels, accelerate process of building models, add more heteroatom chemistry.
- This approach is great for quickly seeing what is predicted by current knowledge of combustion chemistry.
- Sometimes discover serious Discrepancies.
- **Discrepancies motivate ongoing work to improve on current knowledge, and to develop better methods.**



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