

Integrating Fundamental and Applied Combustion Research

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Our Goal

The experimental and theoretical characterization of chemical reactivity in the context of combustion



Fundamental Science in the Context of Combustion

- Novel approaches to quantum chemistry that address current limitations
- New methods for systematic thermochemistry
- Advanced techniques for generating accurate global potential energy surfaces
- New experimental methods for high-temperature chemical kinetics and dynamics
- New perspectives on chemical reaction dynamics and kinetics (roaming, intercepting...)
- New approaches to global sensitivity analysis and uncertainty analysis
- Rational methods for choosing problems and improving combustion models

While the effort is performed in the context of combustion, the work addresses major issues in 21st Century gas-phase chemistry



Connecting Basic and Applied Combustion Research

*Using Chemistry, Engineering, and HPC to drive 21st Century
Combustion Science and Technology*

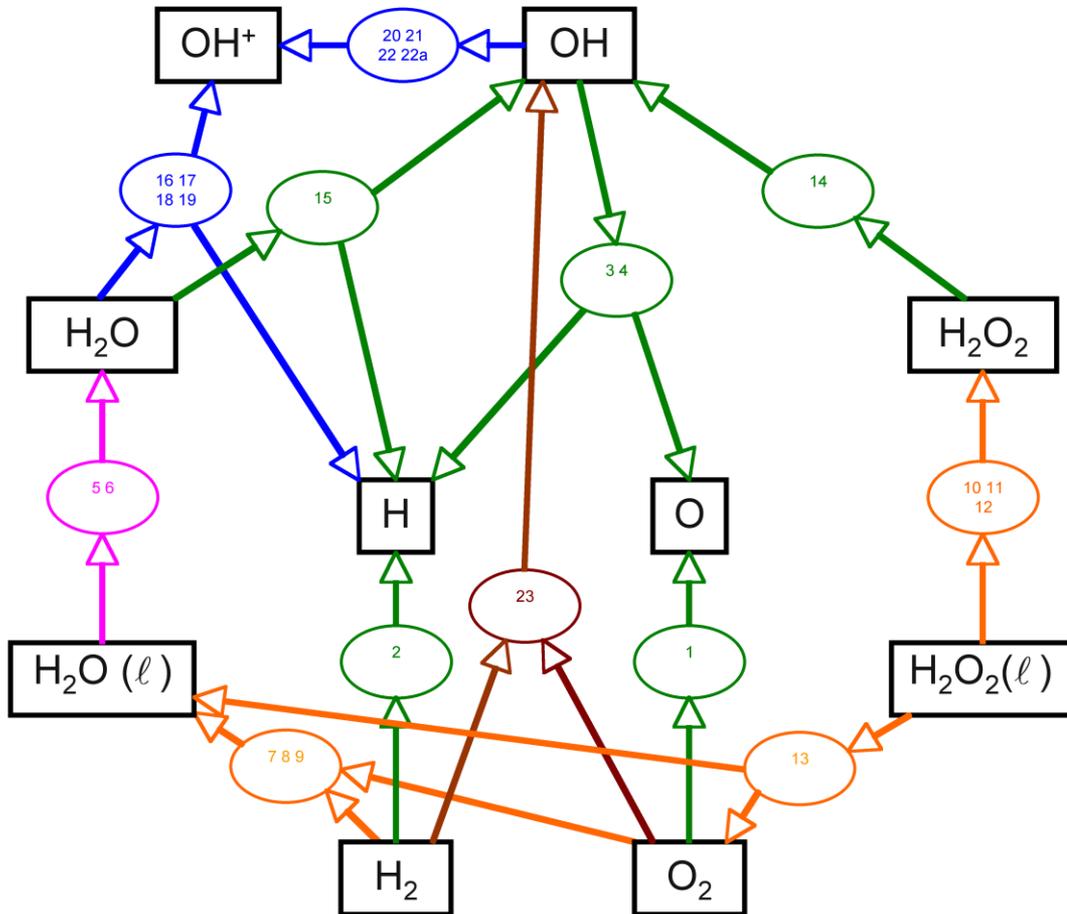
- ★ Coupling large-scale, high-fidelity engine simulations that include detailed fuel chemistry with global sensitivity analysis allows the identification of key chemical and physical parameters whose uncertainties determine the uncertainties in the predictions of the simulations.
- ★ Minimizing the uncertainties in these key parameters through new calculations and experiments can reduce uncertainties in subsequent simulations, and allow the rational improvement of the models and their predictions.
- ★ This approach provides a 21st century, first-principles method to improve combustion simulations and aid the development of new fuels and engines.
- ★ This approach also provides a science-based approach for identifying the most relevant use-inspired problems for future fundamental studies.

Collaborative work within the CSE, ESD, and ALCF at Argonne has already demonstrated the efficacy of the approach, and we are ready to develop its potential on a much larger scale.



Active Thermochemical Tables

Branko Ruscic



A unified approach to the evaluation and compilation of thermochemical data

- Simultaneous optimization of the full thermochemical network
- Consistent propagation of errors
- Instantly updated, allowing incorporation of new data
- Allows what ifs? and suggests key measurements

available on the web at:
<http://atct.anl.gov/>



Miniature, High-Pressure, Ultra-Fast Shock Tube

Robert S. Tranter and Patrick T. Lynch

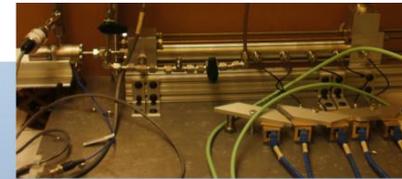
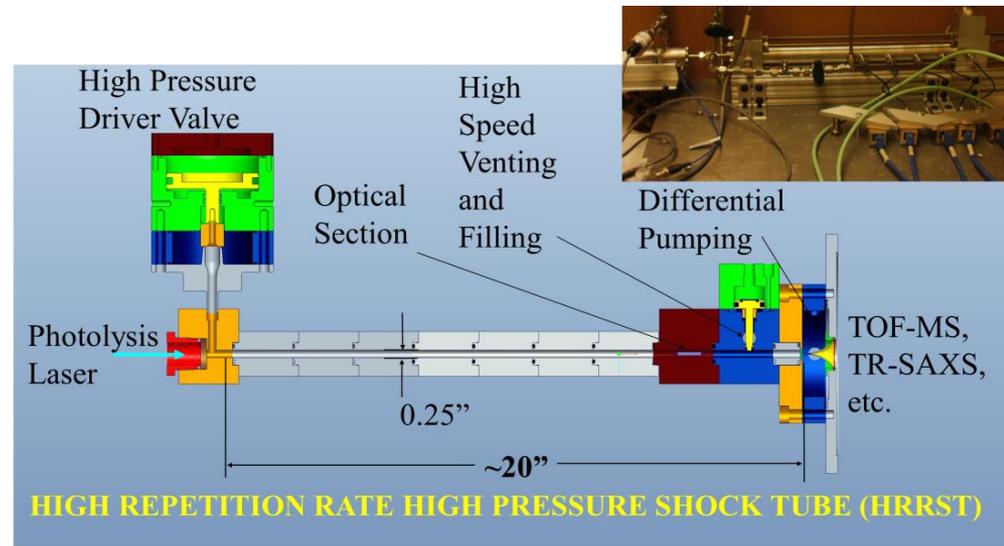
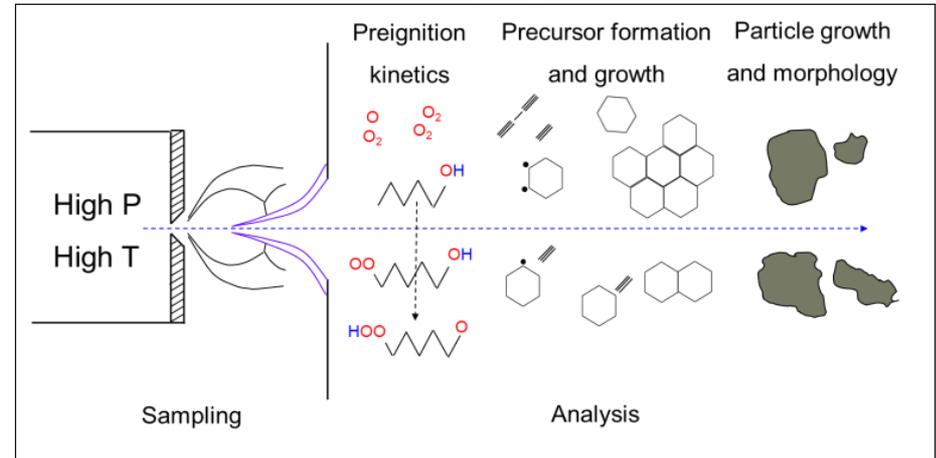
Shock tubes allow the study of high-temperature chemistry but are generally very large (5-10m) and have low repetition rates, making them difficult to use in many environments (e.g., the APS)

A unique mini shock tube has been developed, allowing $P = 10 - 100$ bar; $T = 600 - 3500$ K; Rep-rate > 4 Hz (vs. 1 - 2 per hour for a normal tube).

New design allows advanced diagnostics providing new chemically detailed data.

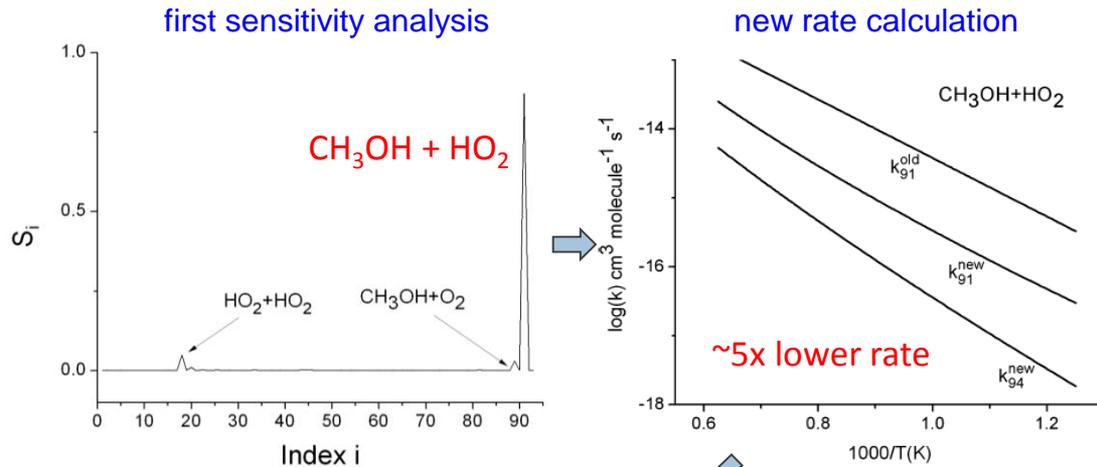
- Time-resolved-SAXS at the APS
- Photoionization TOF-MS at ALS

Molecular beam sampling from shock tube

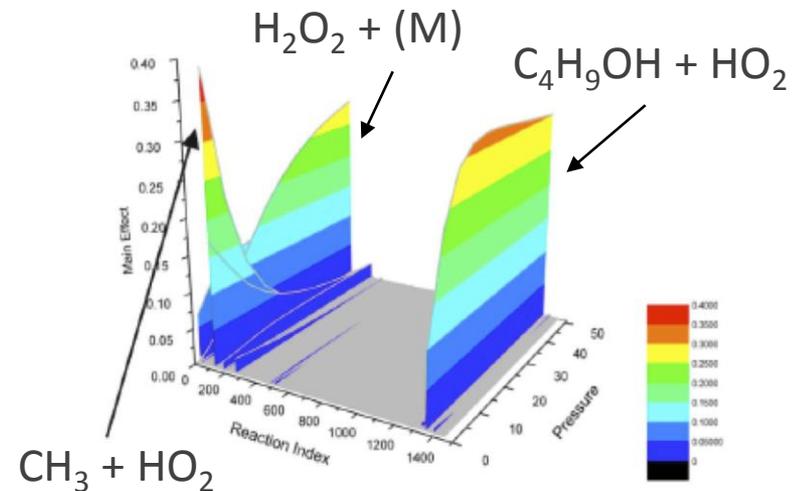
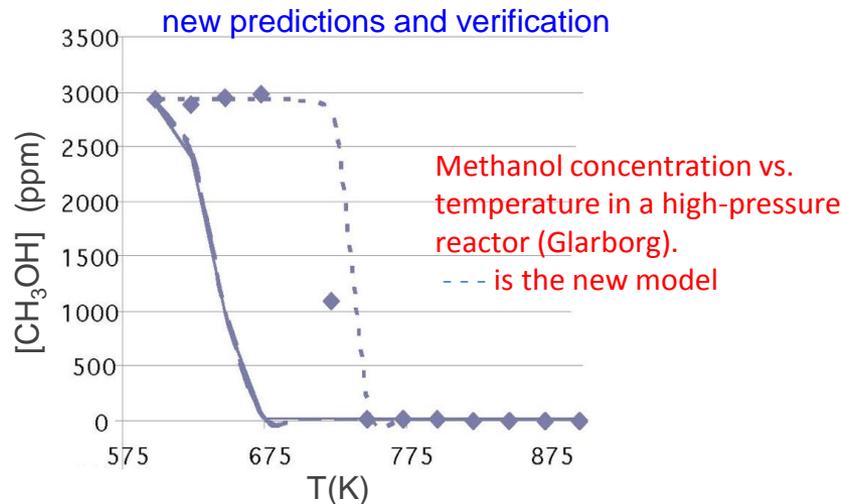


Rational Improvement of Combustion Mechanisms

Realistic models require data for thousands of reactions; only a fraction are validated
Michael Davis, Larry Harding, and Stephen Klippenstein



- Global sensitivity analysis identifies key reactions
- New experiments or theory to provide improved data
- Feedback, iterate, and ultimately automate



Applications to larger systems (butanol)

with D. D. Y. Zhou and R. Skodje (University of Colorado), and A. S. Tomlin (University of Leeds)



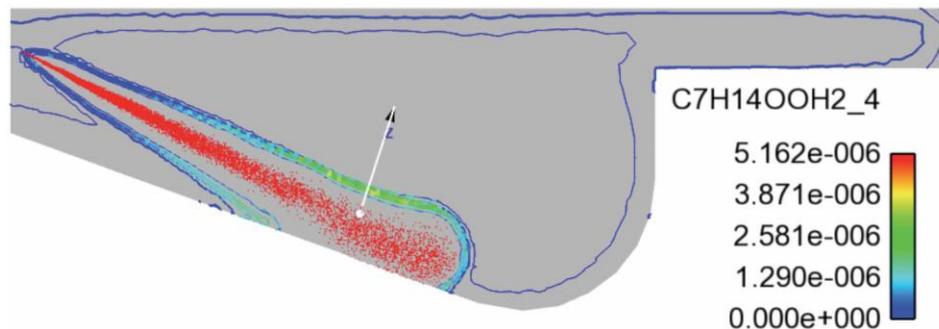
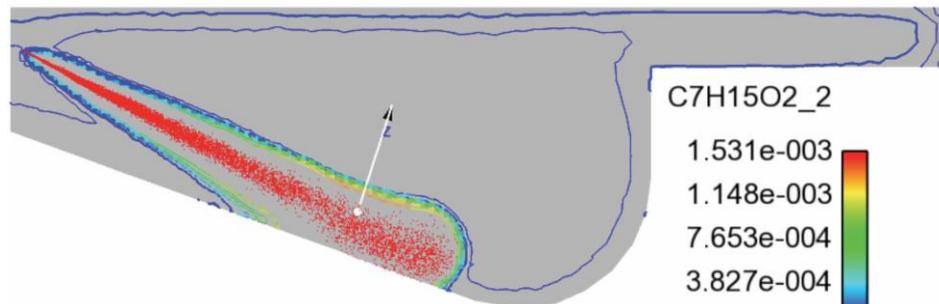
Speciation and Sensitivity Analysis in Engine Simulations

W. Liu, M. J. Davis, R. Sivaramakrishnan, G. M. Magnotti, P. Kundu, S. Som, and D. E. Longman

- Following key elementary reactions under engine conditions:



- Temperature contours show where and when these reactions are important
- Significant reduction in simulations necessary for sensitivity analysis



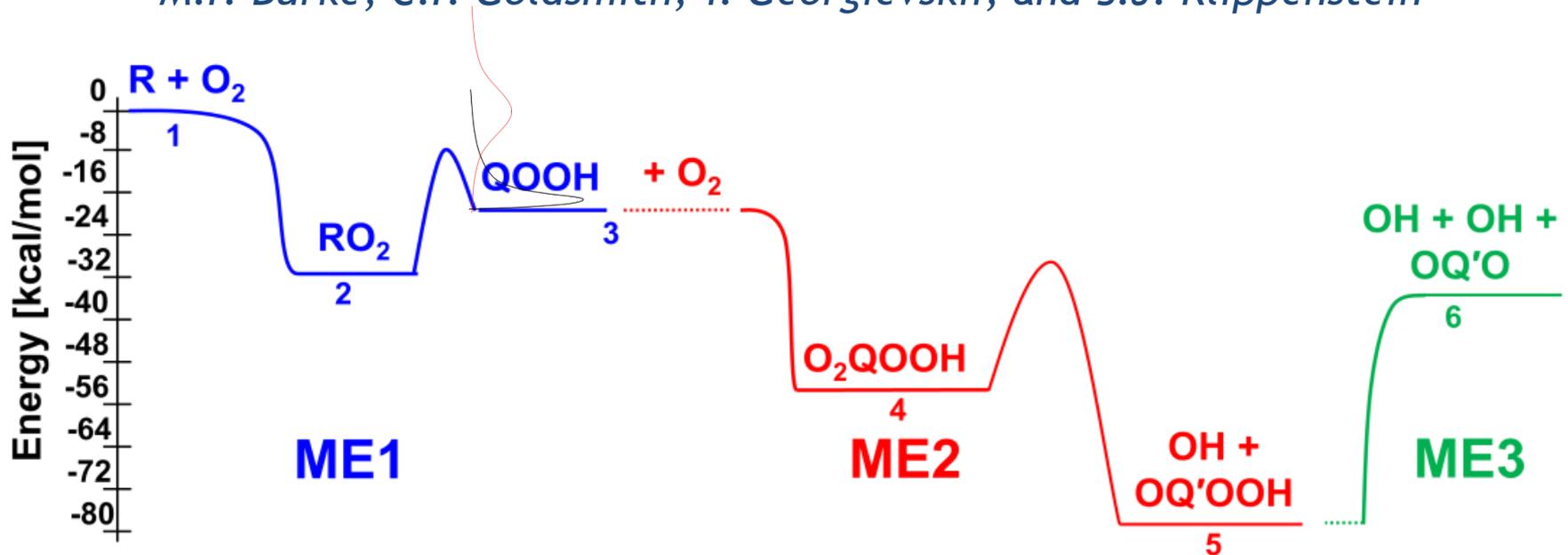
- Engine simulations with global sensitivity analysis identify both the important reactions and the conditions under which they must be well-characterized.
- Directly couple fundamentals to end use.



Understanding the Role of Non-Boltzmann Reactant Distributions in Low-Temperature Oxidation

Reactions of thermalized and hot reactants may display very different kinetics

M.P. Burke, C.F. Goldsmith, Y. Georgievskii, and S.J. Klippenstein



- Standard approach assumes products are thermalized before undergoing next reaction
- In some instances, reactants are still "hot" and the subsequent rates are affected
- A method was developed to treat this situation through a series of coupled master equations
- The method allows the determination of rate coefficients, $k(T,P,X_{O_2})$, for combustion modeling

Factor of three differences in OH predictions at conditions commonly used to study low-temperature combustion



Dinner?

