The Oxidation and Autoignition of Jet Fuels

Matthew Oehlschlaeger

Mechanical, Aerospace, and Nuclear Engineering
Rensselaer Polytechnic Institute, Troy, NY

Sponsor: AFOSR, Dr. Chiping Li

Motivation: changing fuel supply

- Combustion properties….
  - are dependent on fuel composition
  - of low-volatility and alternative fuels are less well characterized

Methodology

- Shock tube studies as high-pressures for fuel/air mixtures (engine-like conditions)

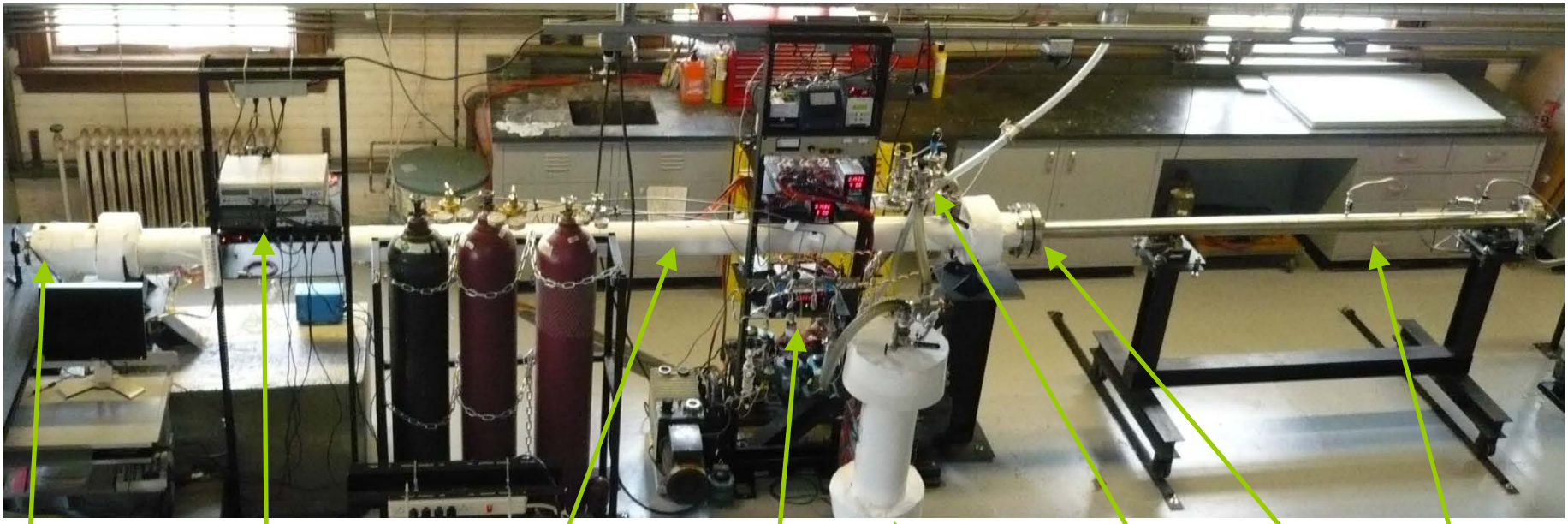
Payoff

- Quantitative targets for the validation of kinetic models
- Direct comparisons of fuel reactivity

Methodology: heated shock tube technique

- Isolation of homogenous gas-phase kinetics
- Reactants are heated “instantaneously”
  - Zero-dimensional model
  - Temperature and pressure can be accurately determined (typ. 1-2% uncertainties)
- High pressures achieved behind reflected shocks
  - Present studies ~7-50 atm
- Extended test times (10 ms) achieved using tailored driver gases

RPI shock tube facility



Shock velocity detection

Mixing manifold

Vacuum section

Driver

Test location w/ optical access

Heated and insulated driven section

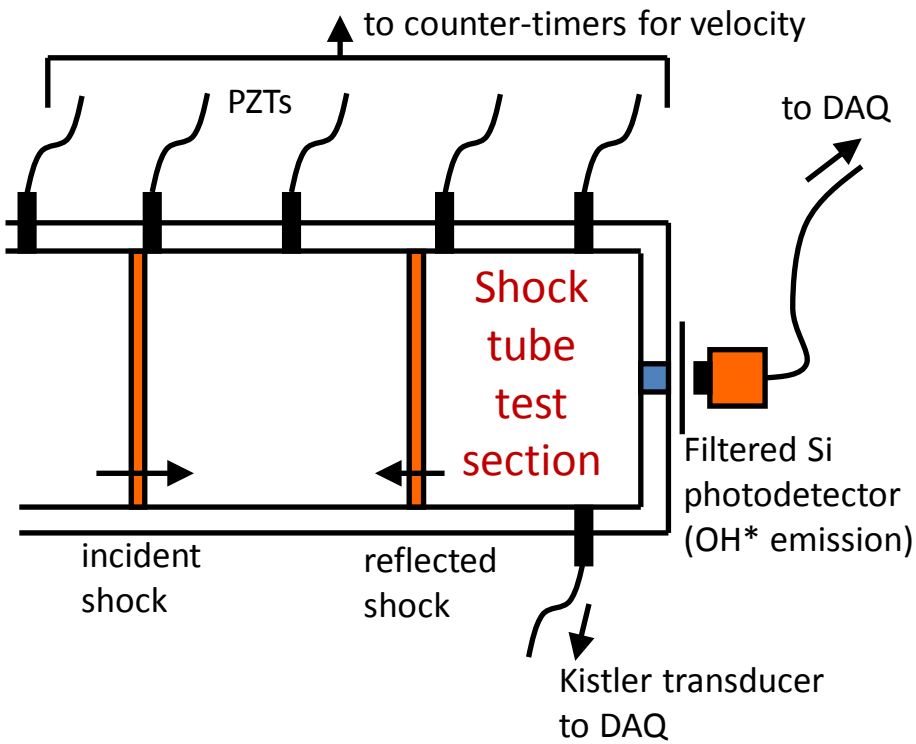
Heated and insulated mixing vessel

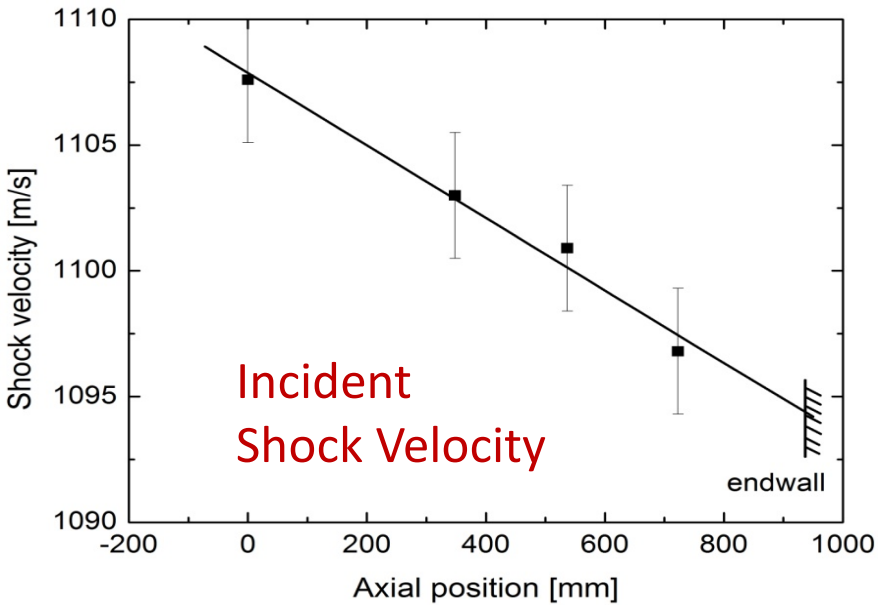
Diaphragm

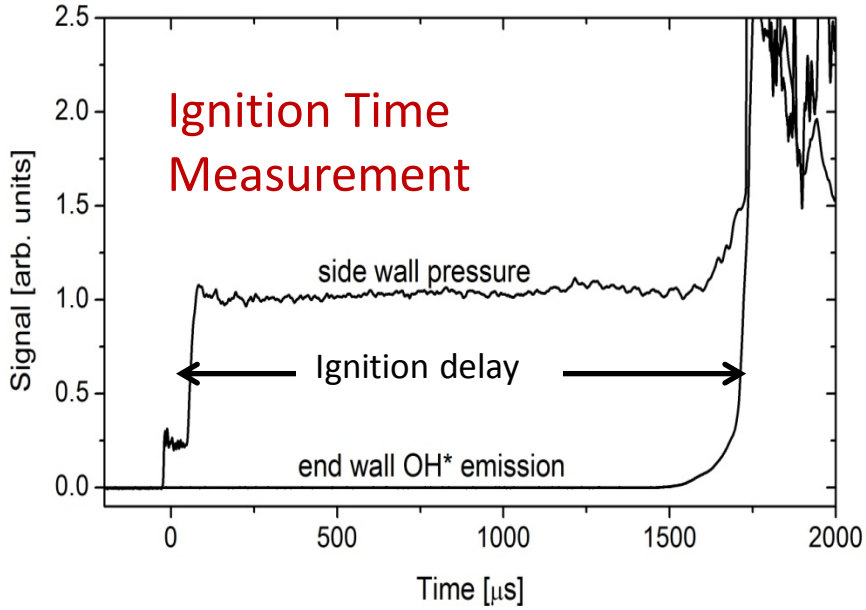
Inner diameter = 5.7 cm; initial temperatures up to 200 C

Condition Space	P [atm]	T [K]	τ [ms]	ϕ
Accessible	1 - 200	650 +	0 - 10	
Typ. for fuel/air	5 - 60	650 - 1300	0.05 - 10	0.25 - 2.0

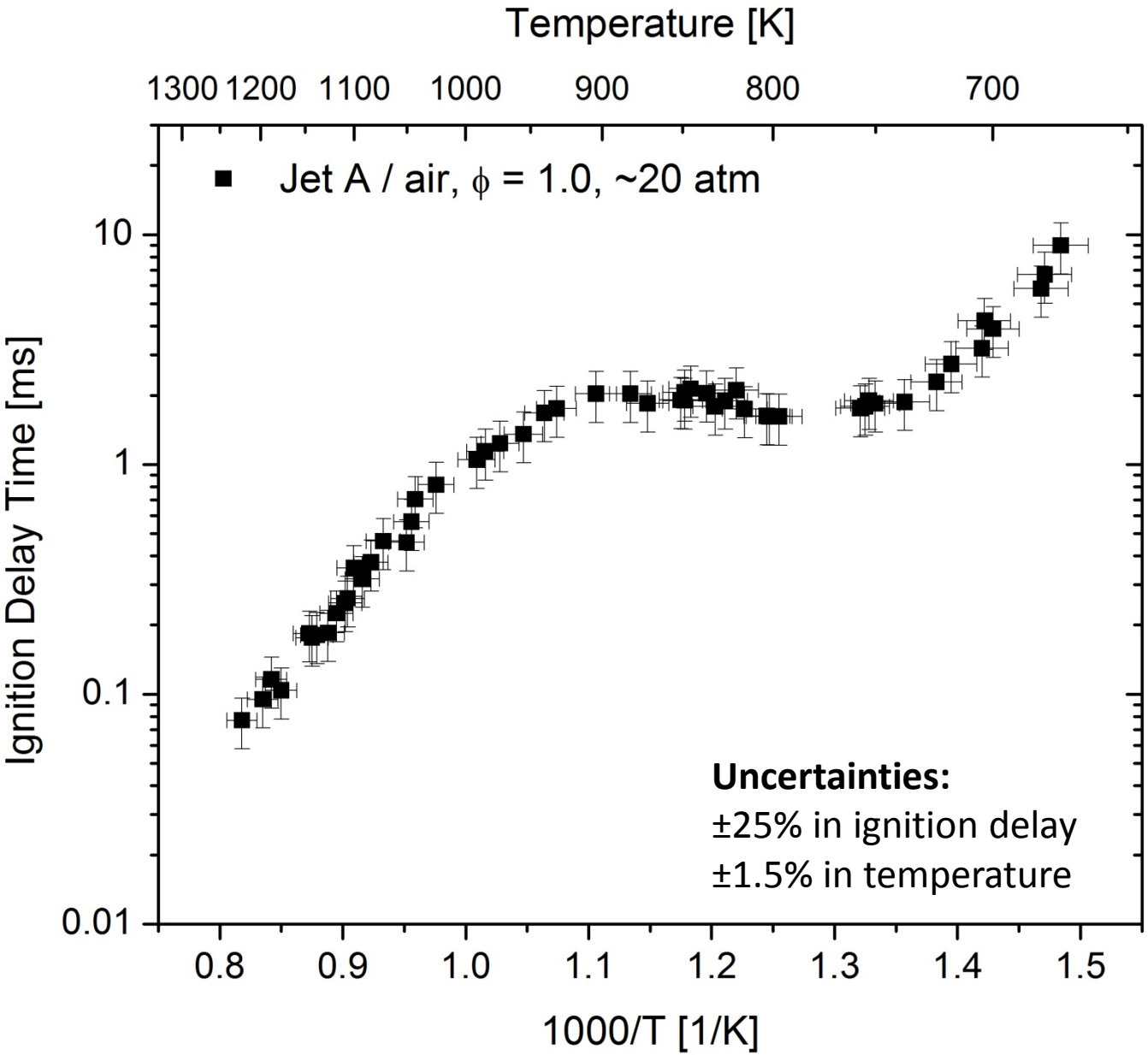
Ignition delay measurement



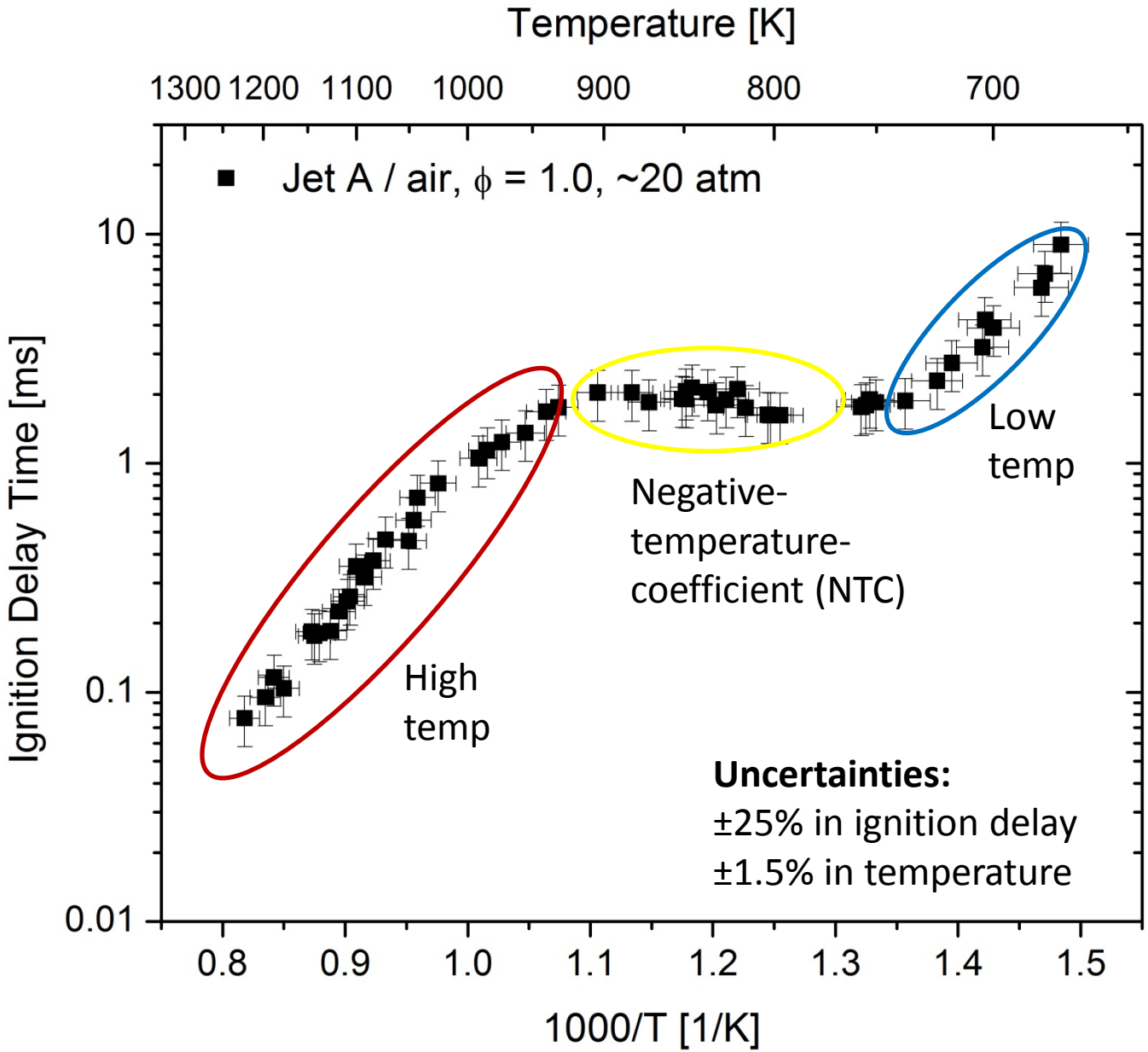




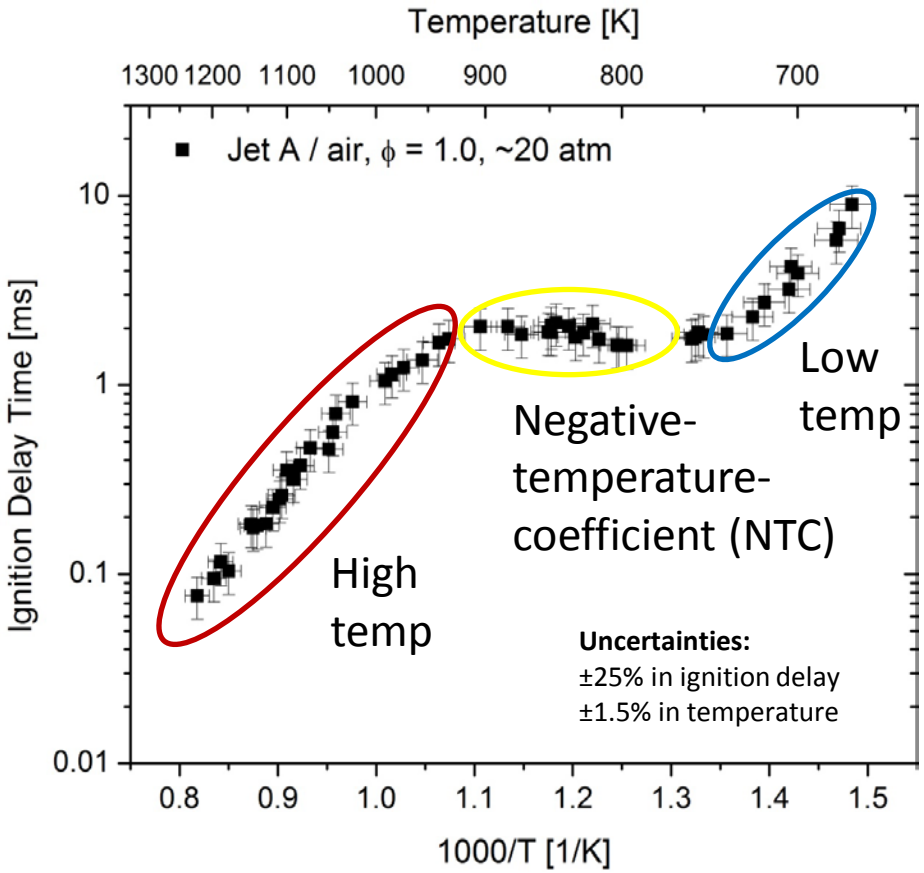
Example results

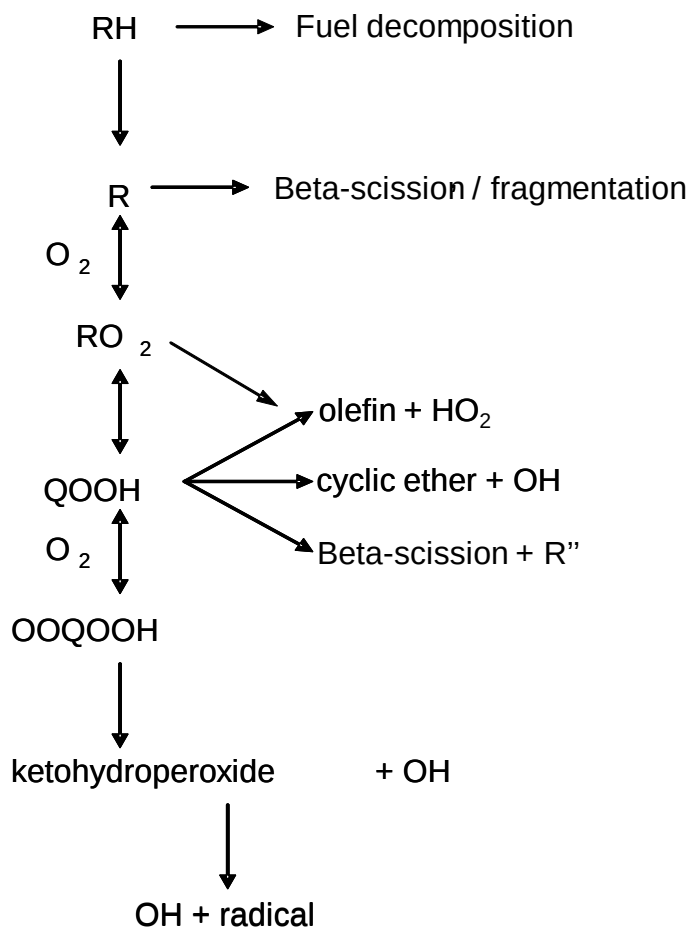


Example results



Example results

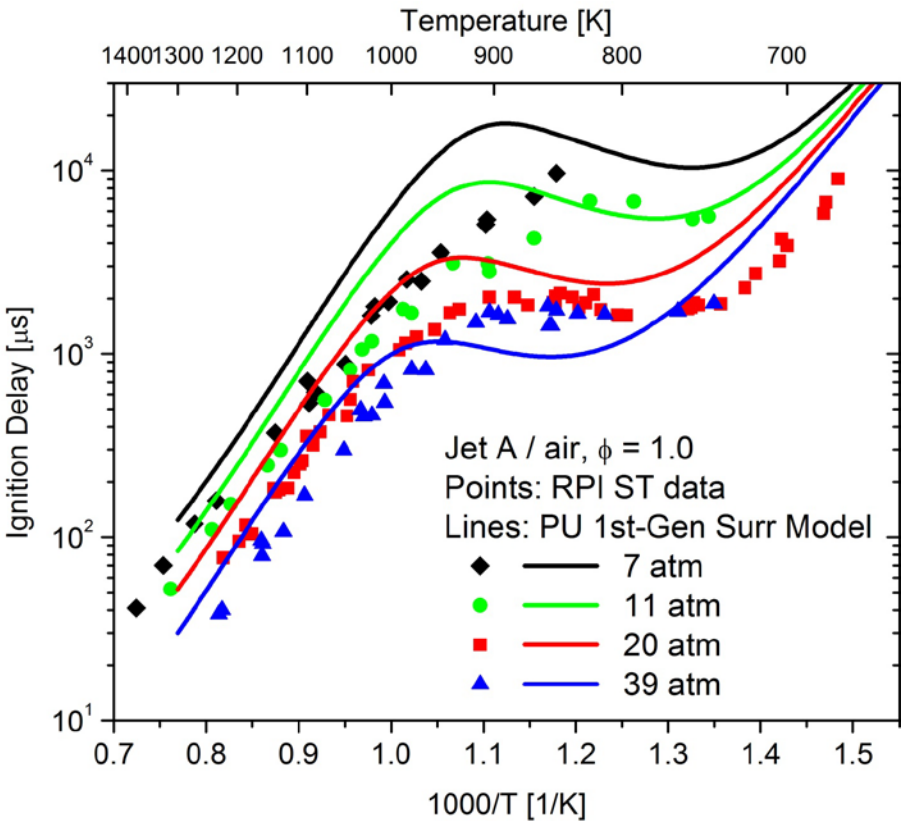




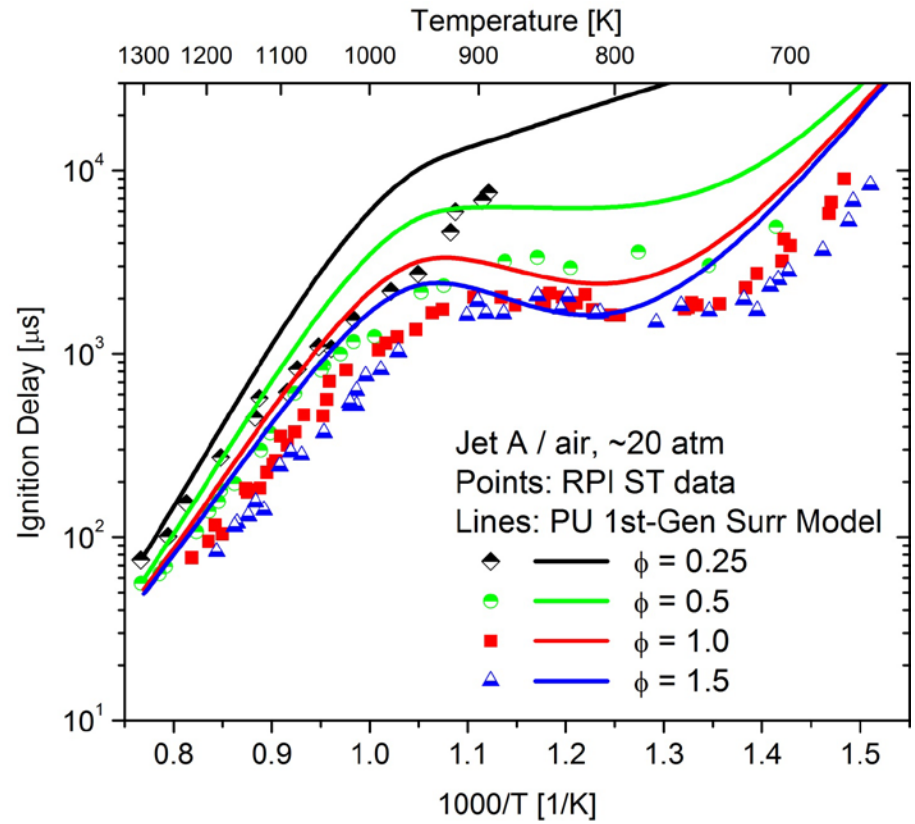
- Temperature dependence mechanistically explained by models in literature
- Quantitative prediction is a work in progress

Experiment vs surrogate modeling

pressure dependence



ϕ dependence

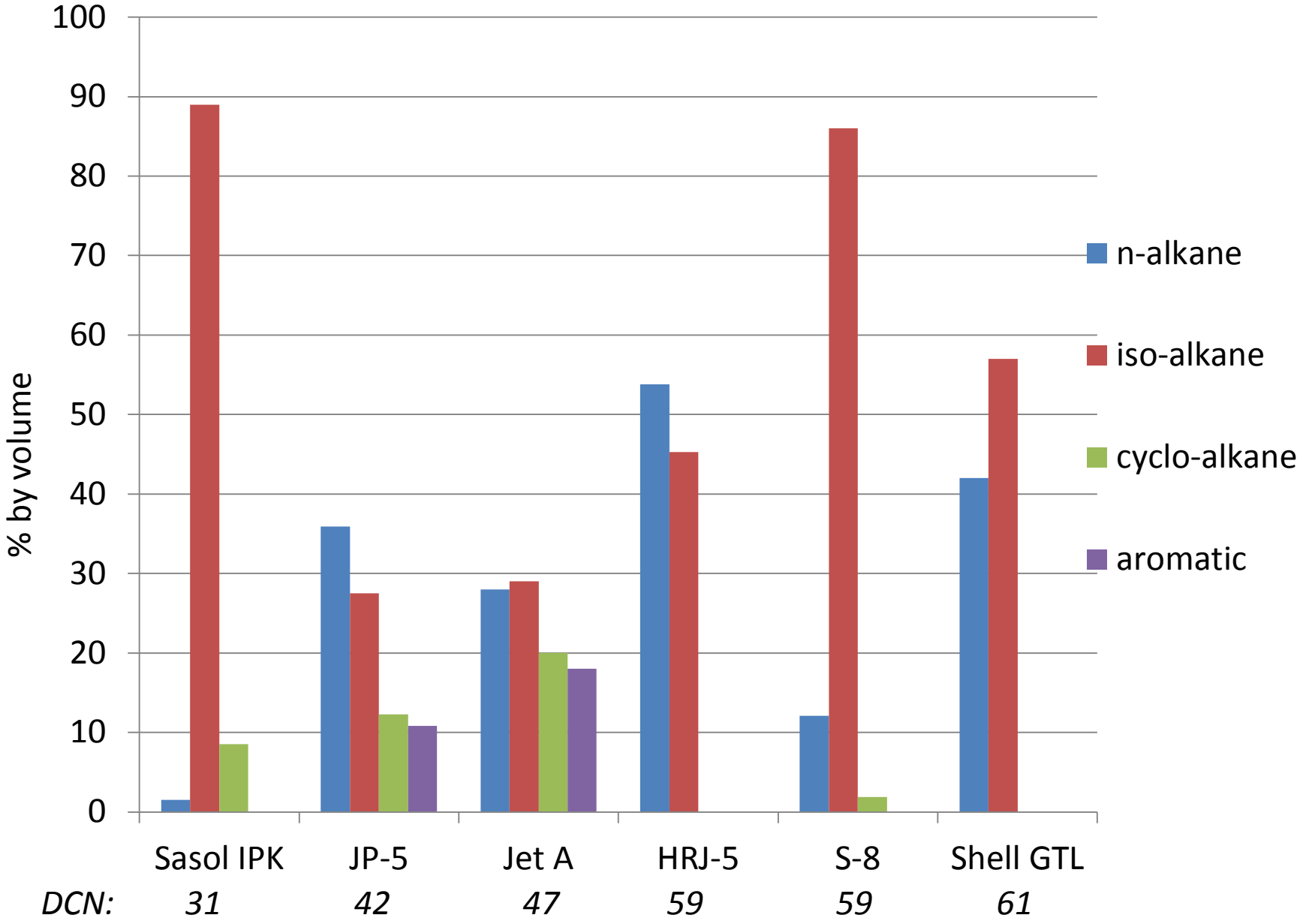


Generalizations

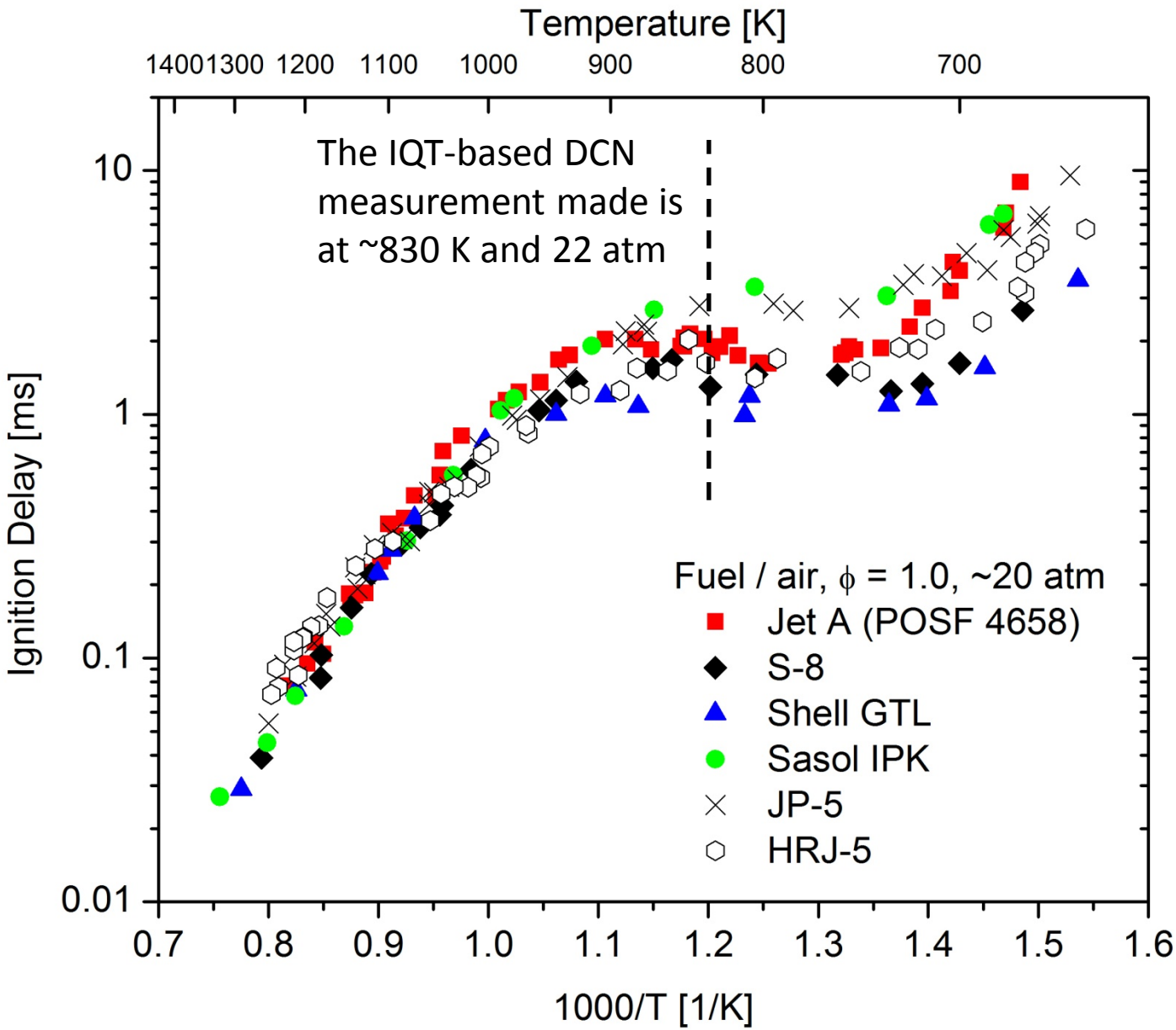
- *a priori* surrogate kinetic modeling deviates with real fuel ignition delay by on average a factor of two – sufficient for "engineering accuracy"?

- Kinetic sensitivities/dependencies much larger in NTC than high-T regime
  - In condition and fuel composition/structure parameter spaces

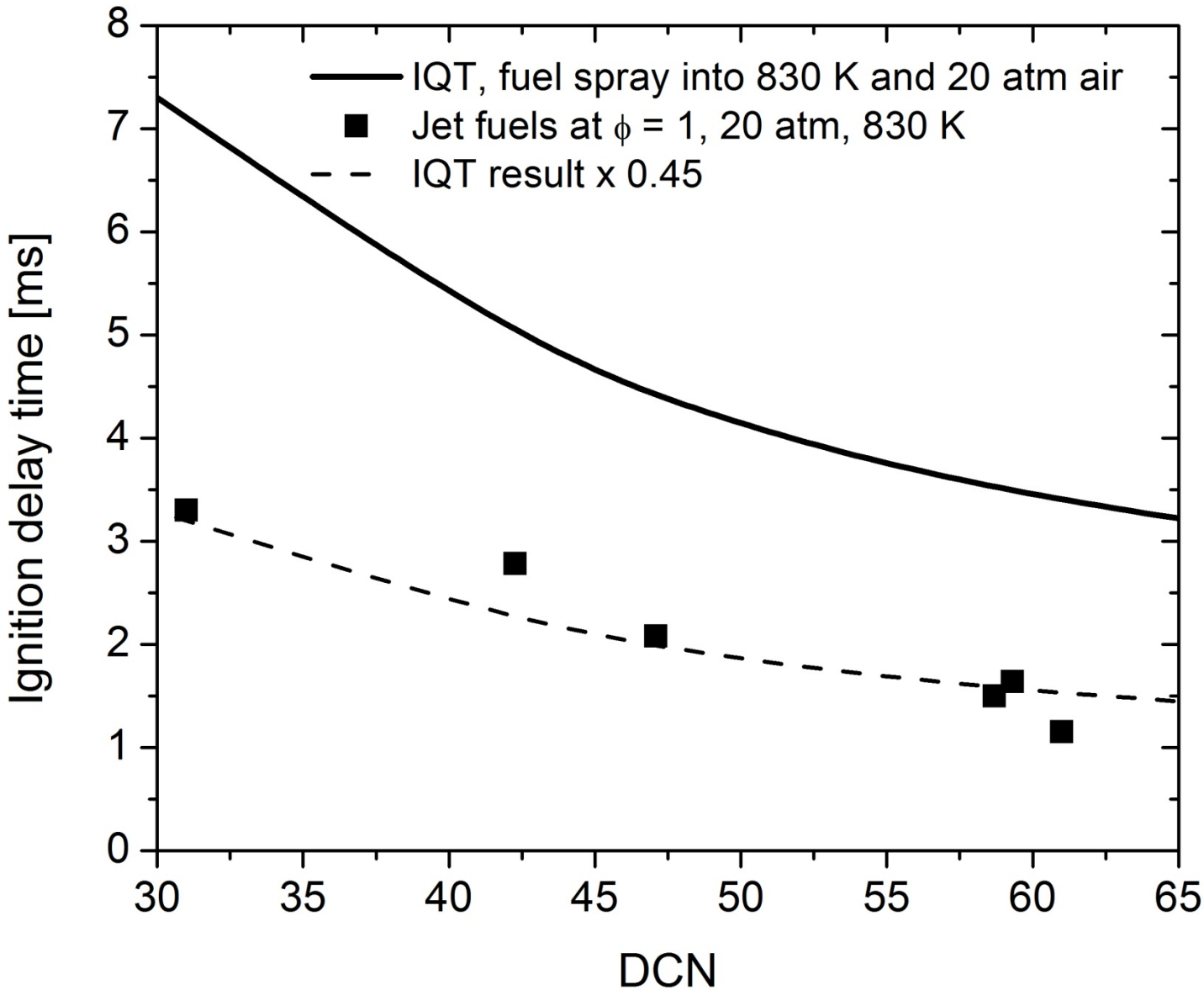
Jet fuel ignition variability



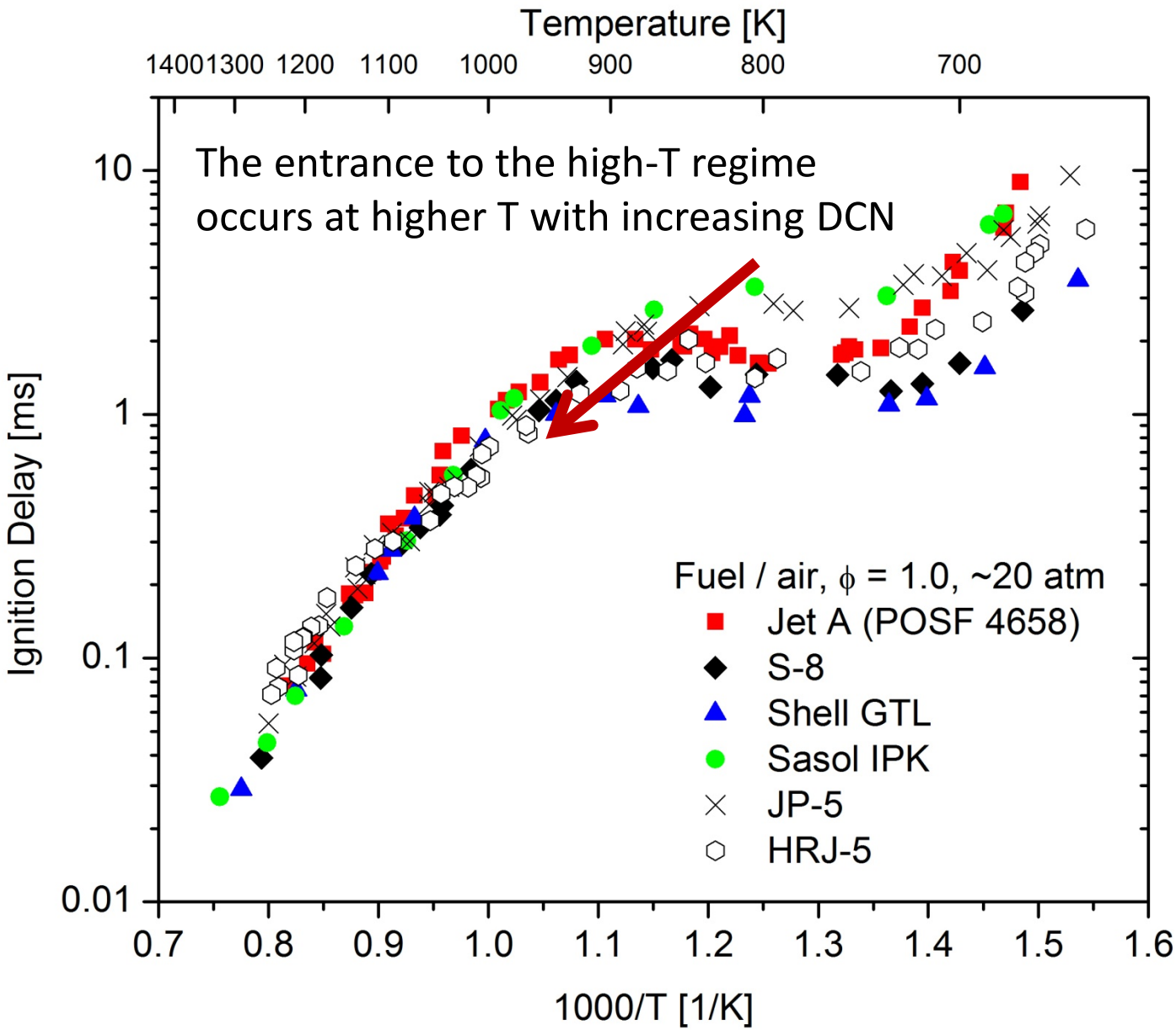
DCN a proxy for NTC ignition delay?



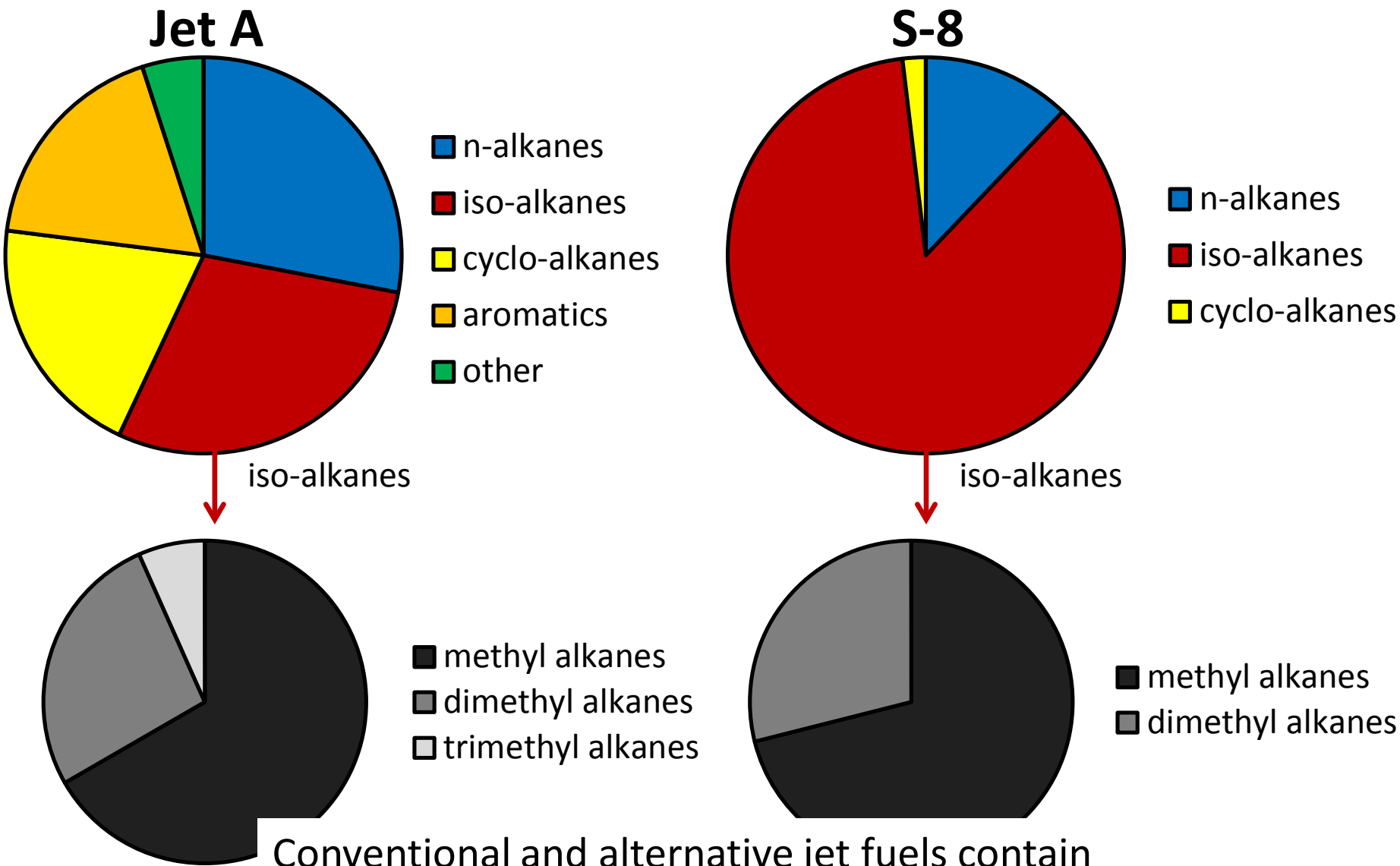
Ignition delay vs DCN



Ignition delay vs DCN



Jet fuel composition

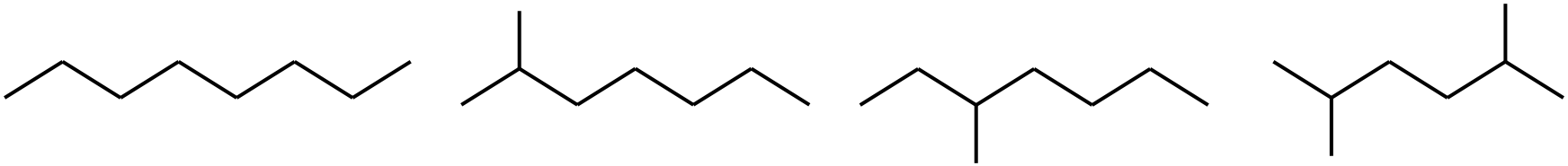


Conventional and alternative jet fuels contain
Large quantities of lightly branched alkanes

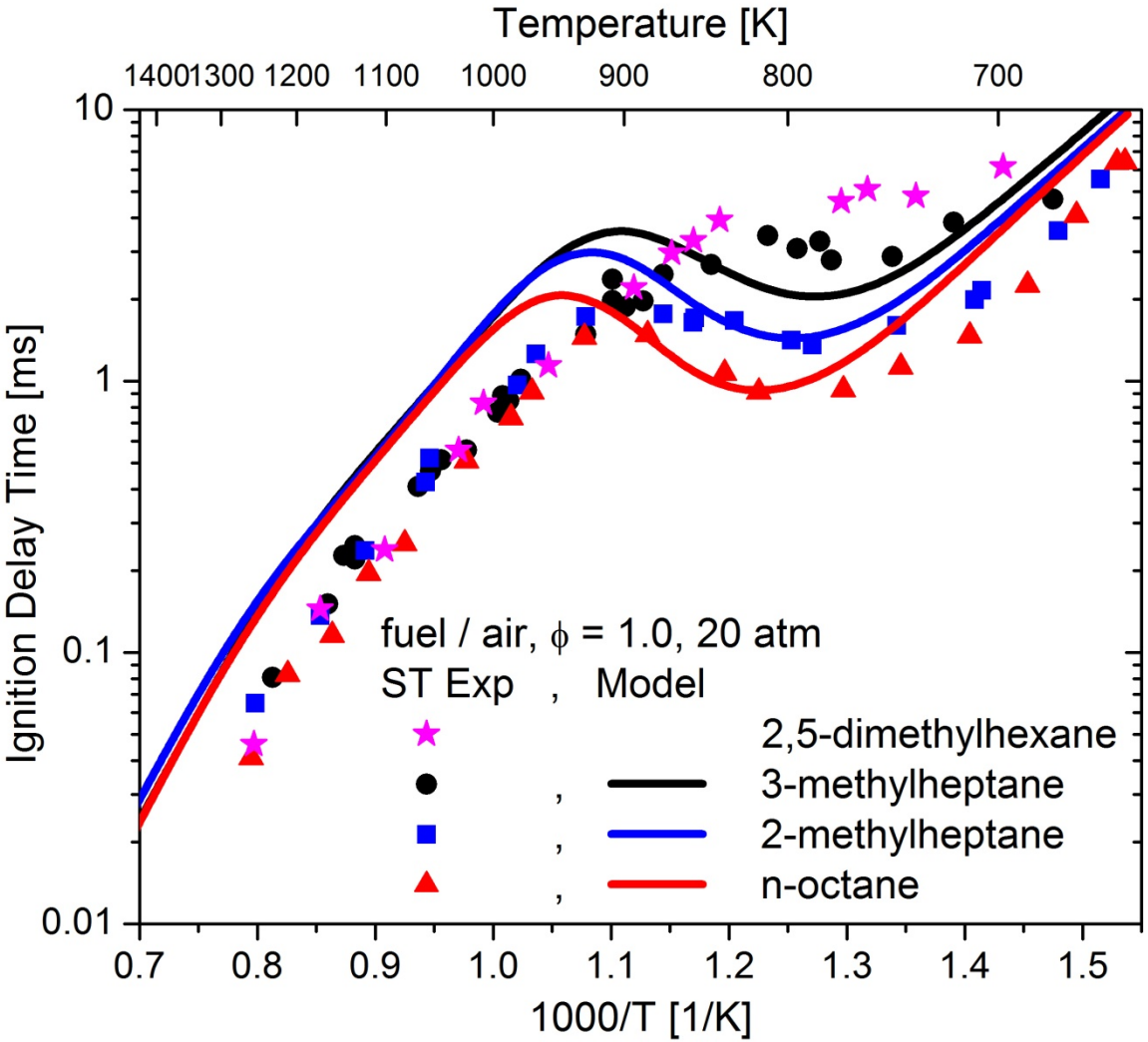
Collaborative study of lightly-branched alkanes

- RPI: shock tube ignition delay
- Nat. Univ. Ireland Galway: shock tube and RCM ignition delay
- LLNL: kinetic modeling

- Compounds studied:



C_8 alkane comparison



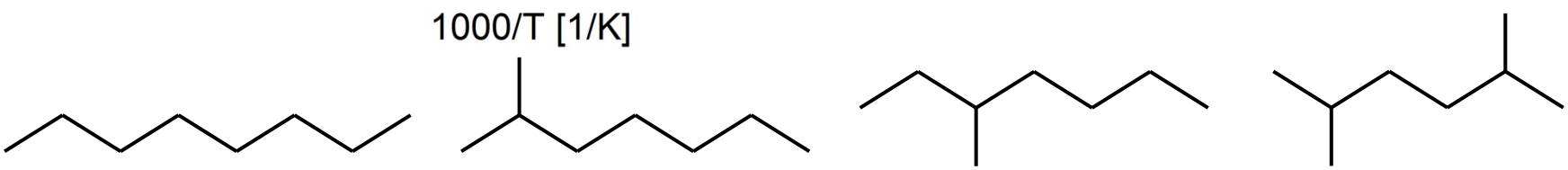
At high-pressure fuel/air conditions

Branching has:

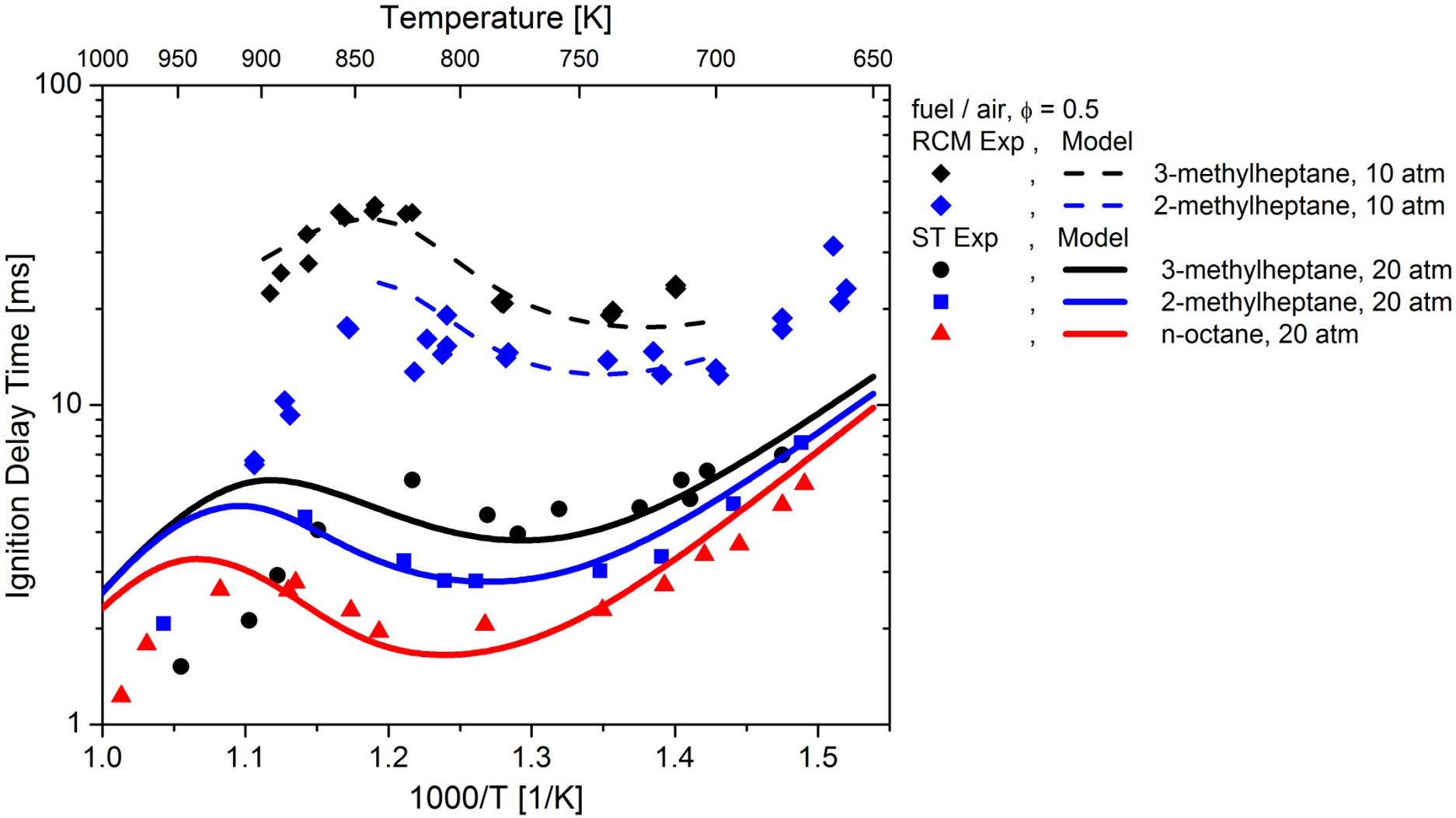
- little to no influence at high T
- significant influence in NTC region

→ dependence on number and location of methyl substitutions

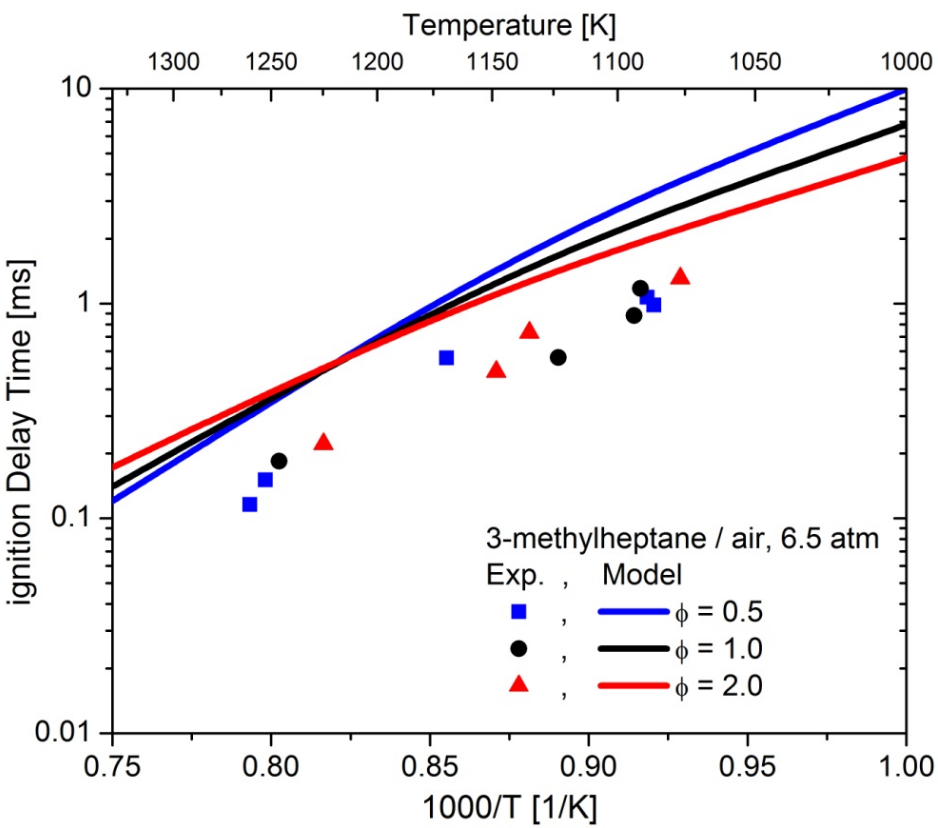
Compound	RON	DCN
2,5-dimethylhexane	56	
3-methylheptane	37	43
2-methylheptane	22	53
n-octane	-19	64

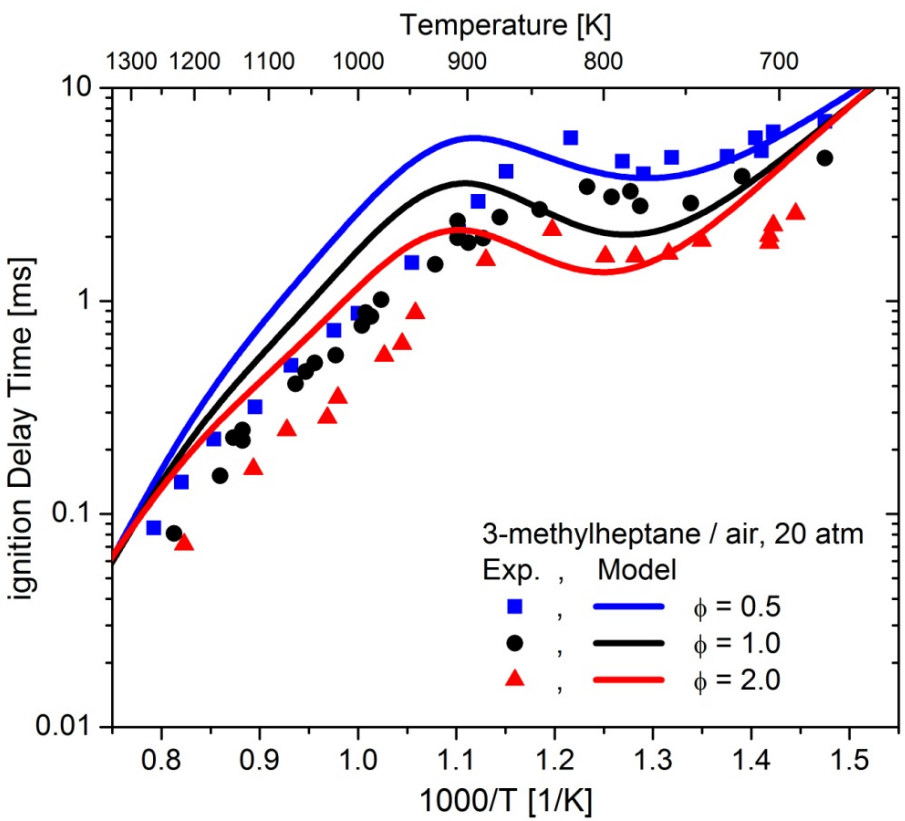


C_8 alkane comparison: T < 1000 K



Equivalence ratio dependence: 3-methylheptane





Higher temperatures

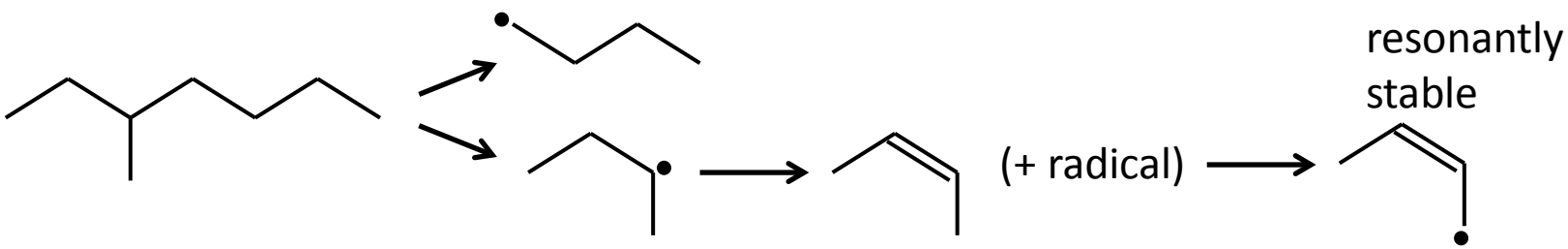
- small ϕ-dependence; crossover in ϕ-dependence at 1200 K for 6.5 atm case

Moderate to low temperatures

- larger ϕ-dependence

Crossover in ϕ-dependence

- T > 1200 K: ignition controlled by $H + O_2 \rightarrow OH + O$
  - Increased ϕ, increased fuel scavenging of H atoms: $fuel + H \rightarrow R + H_2$
- T < 1200 K: $H + O_2 + M \rightarrow HO_2 + M$ competes
  - Increased ϕ, increased radical production: $fuel + HO_2 \rightarrow R + H_2O_2$, $H_2O_2 + M \rightarrow 2OH + M$
- Additionally at T > 1200 K: inhibitive decomposition

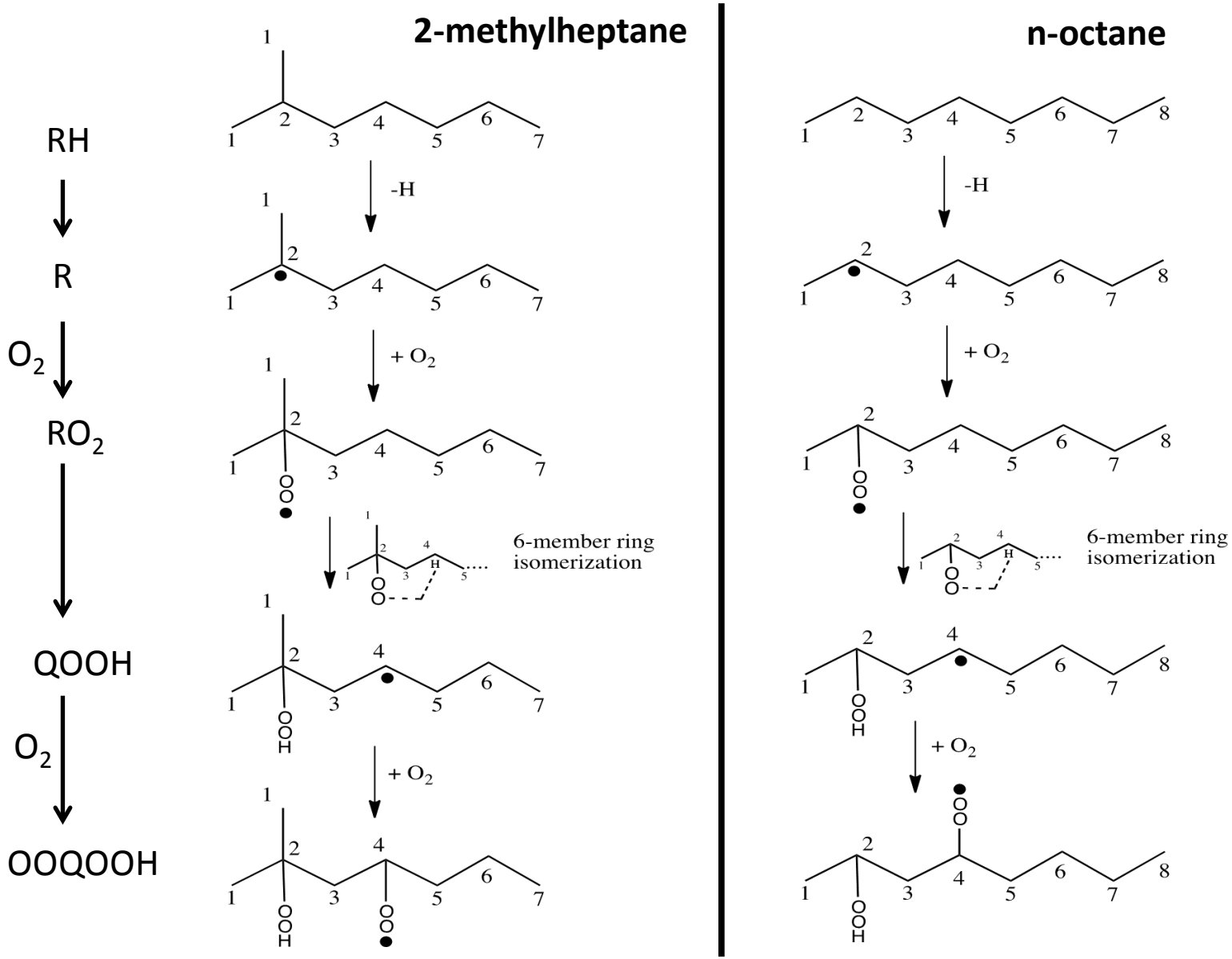


Observations from C_8 alkane isomer studies

- High temperatures
  - Little to no difference in ignition delay for C_8 isomers
    - Similar bond strengths, similar intermediate pool, similar reactivity
  - Model captures pressure- and ϕ-dependence but is ~2x longer than measured ignition delay

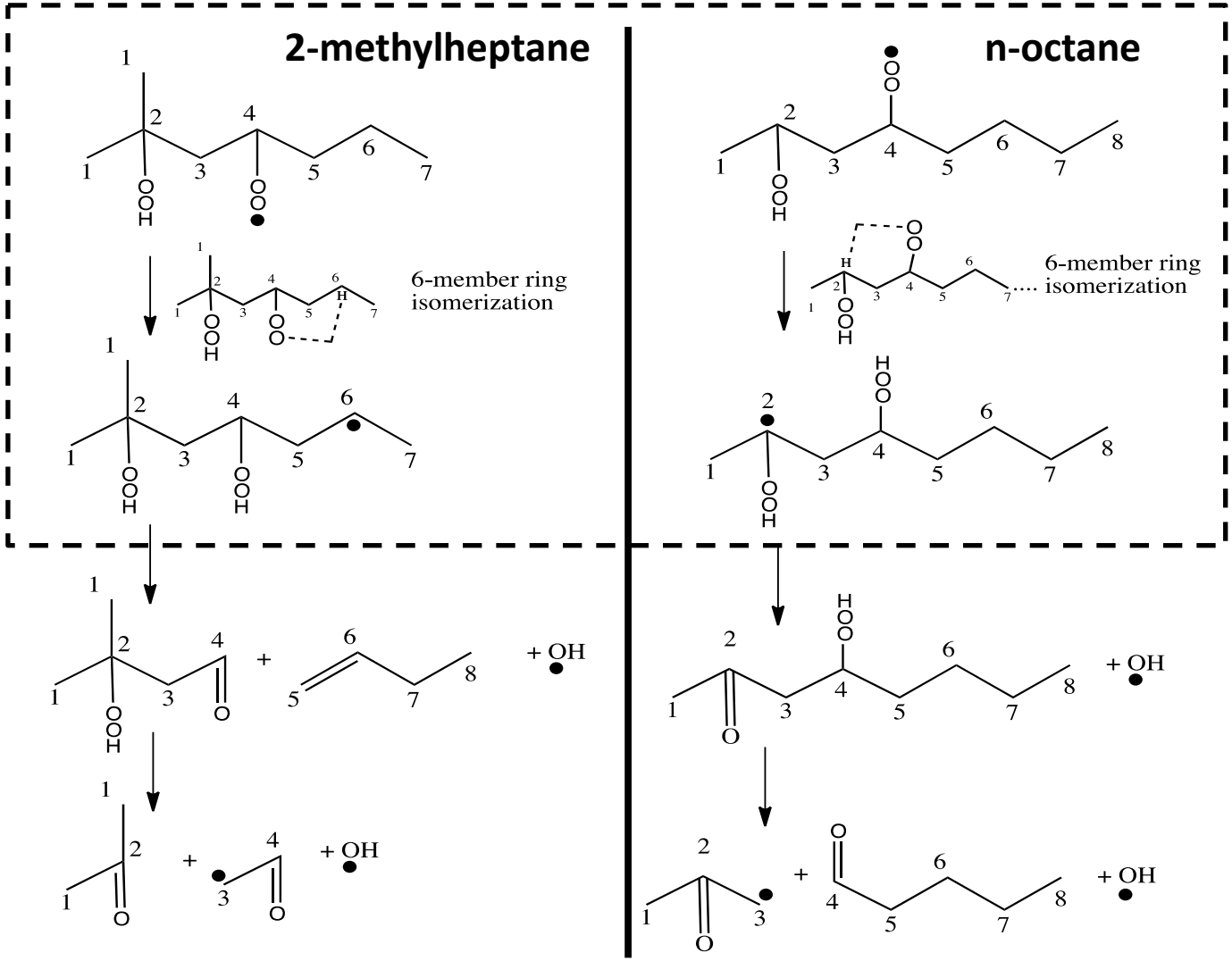
- Low temperatures
  - Model in better agreement with both RCM and ST data
  - Reactivity dependent on location and number of methyl substitutions

Low-T chemistry: 2-methylheptane vs n-octane

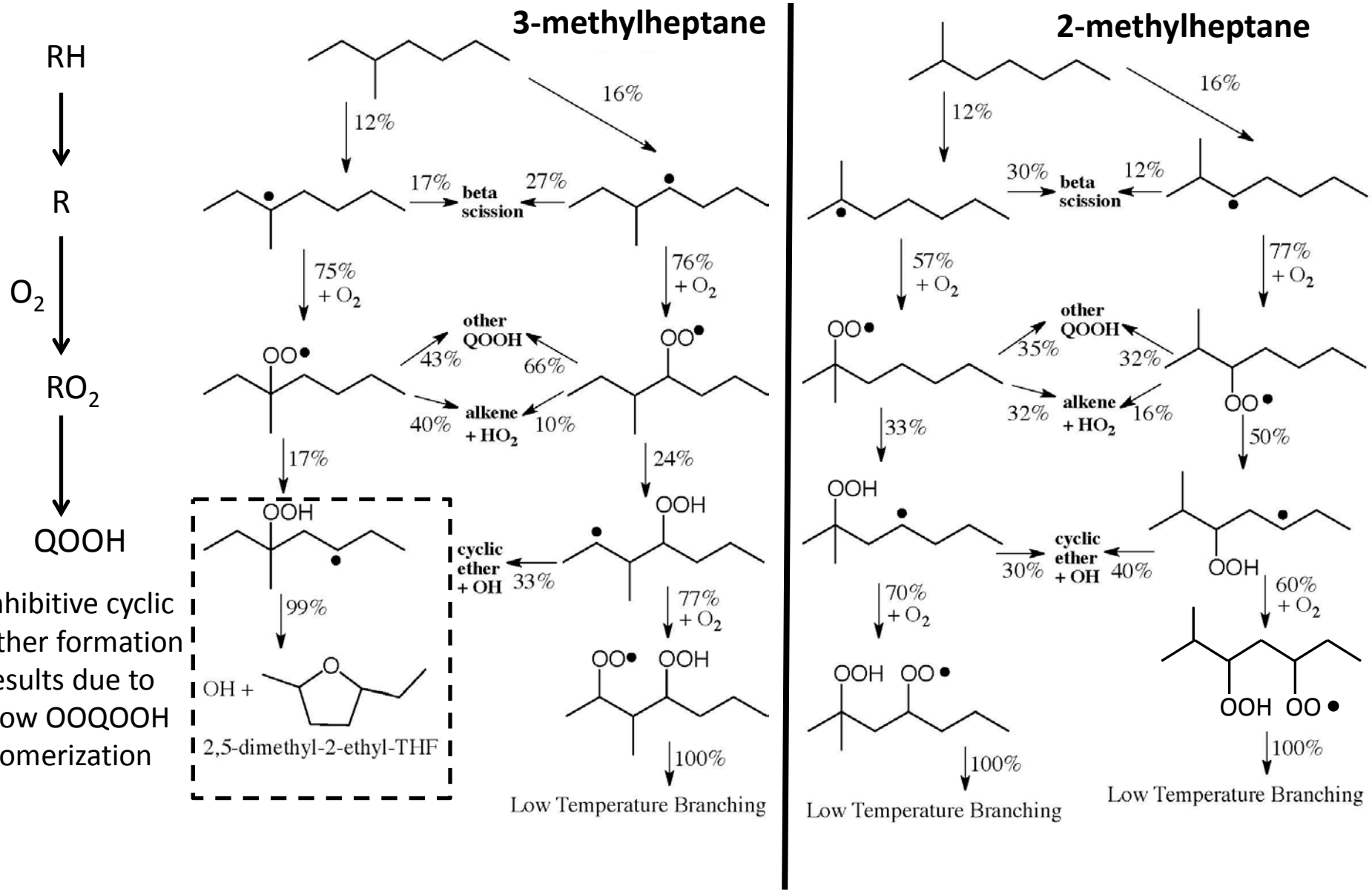


Low-T chemistry: 2-methylheptane vs n-octane

2-methylheptane: slower OOQOOH isomerization; no H atom available at OOH site

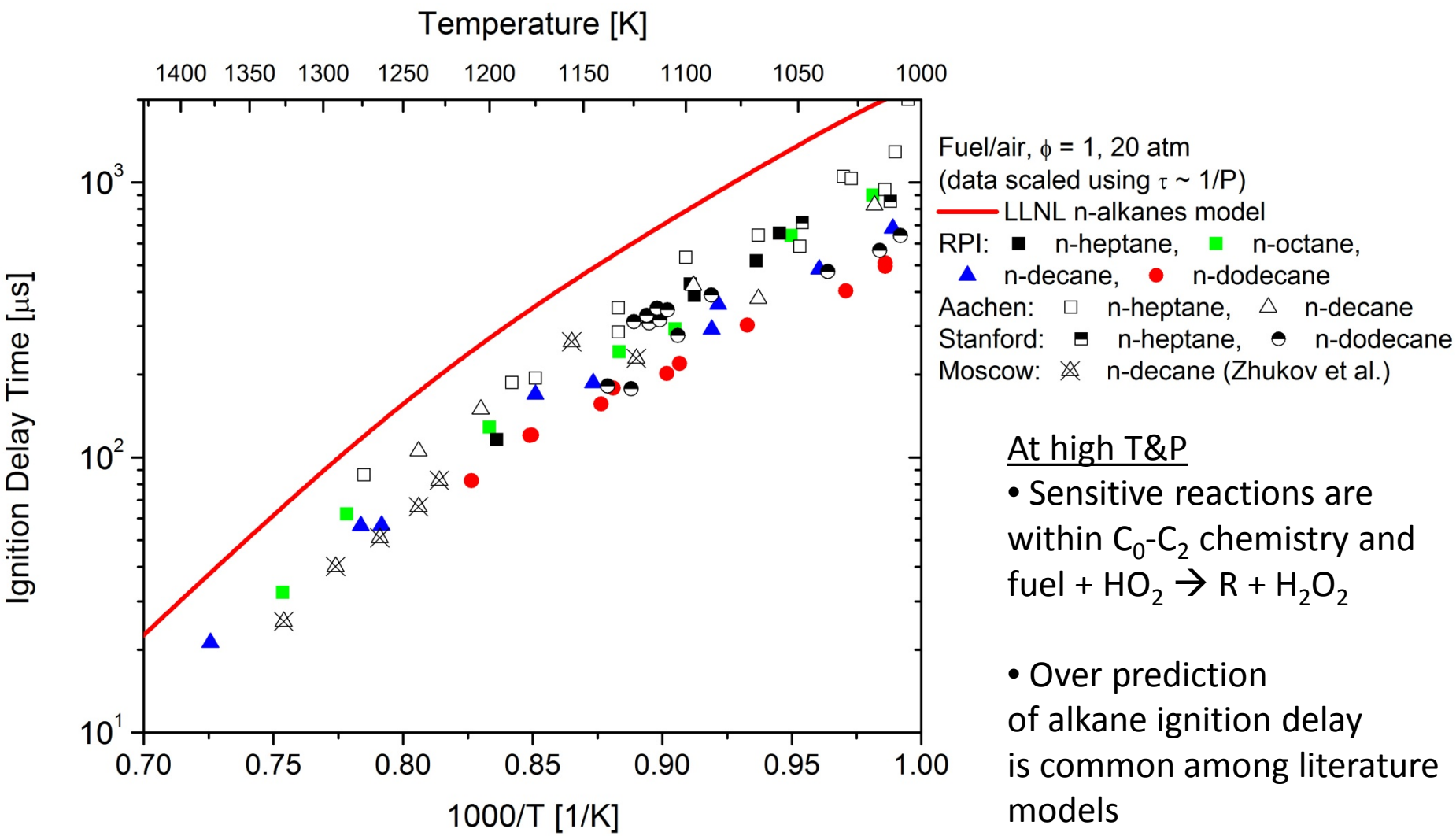


Low-T chemistry: 3-methyl vs 2-methyl heptane



Inhibitive cyclic ether formation results due to slow OOQOOH isomerization

High-temperature deviations



<u>At high T&P</u>

- Sensitive reactions are within C_0-C_2 chemistry and fuel + HO_2 → R + H_2O_2

- Over prediction of alkane ignition delay is common among literature models

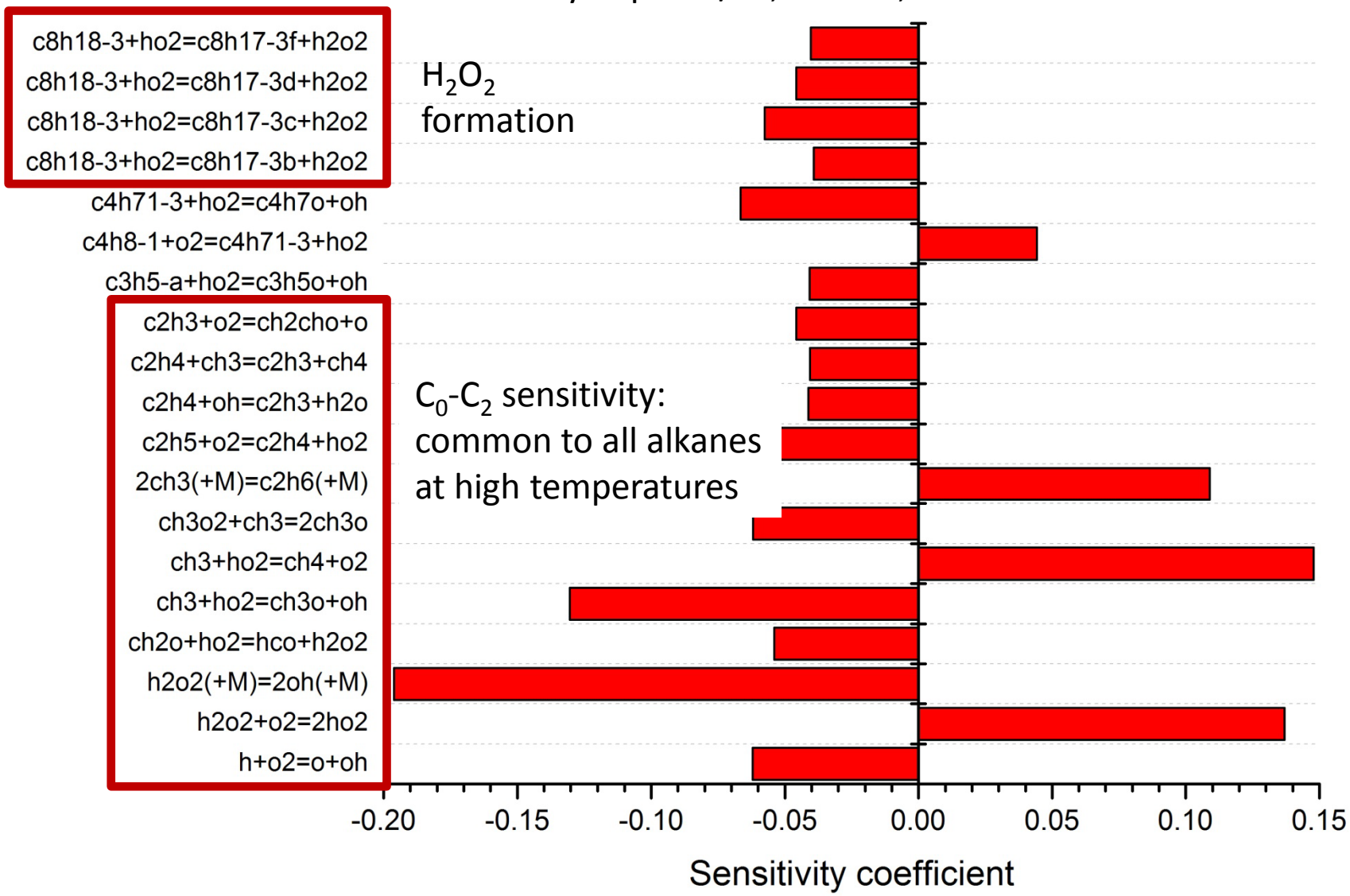
Summary

- Jet Fuels
  - Ignition delay variability large in the NTC
  - Correlates with DCN
    - Not yet clear how universal this observation is

- Normal and lightly-branched alkanes
  - Number and location of methyl substitutions has a strong influence on NTC ignition delay
  - Isomer reactivity differences explained by competition among low-T radical branching and propagation pathways
  - Perhaps still some issues with high-T alkane kinetics

Acknowledgements

- RPI: Dr. Haowei Wang, Weijing Wang
- LLNL: Drs. Bill Pitz, Charlie Westbrook, Mani Sarathy, and Marco Mehl
- Princeton: Drs. Fred Dryer, Yiguang Ju, Stephen Dooley, and Sang Hee Won
- NUI Galway: Drs. Henry Curran and Darren Healy
- AFOSR (sponsor): Dr. Chiping Li

Sensitivity analysis

3-methylheptane/air, 20 atm, 1100 K