Chemical kinetic modeling development and validation experiments for direct fired sCO2 combustor

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Project Summary

Develop a chemical kinetic mechanism for Supercritical Carbon Dioxide (sCO_2) Mixtures

Validate the chemical Kinetic Mechanism with shock tube experiments

Develop a CFD Code that utilizes mechanism for sCO_2 combustors

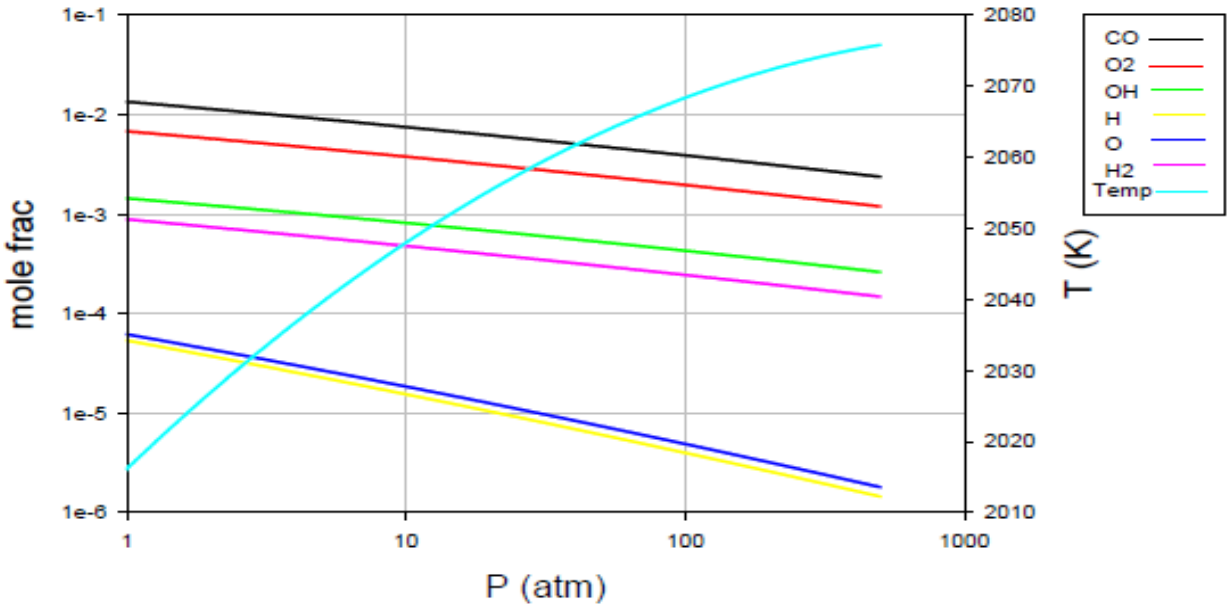
Motivation

Current state-of-the-art, such as GRI-3.0 Mechanism, has only been validated for pressures up to 10 atm

Mechanisms have not been developed for CO_2 diluted mixtures

Updated mechanism will allow for accurate combustor modeling with multi-step combustion using a validated mechanism

Current CFD combustion models do not consider non-ideal effects



Effects of Increasing Pressure. Equilibrium calculation for $CH_4/O_2/CO_2$ at $\phi = 1$. Figure adapted from Strakey, 2014, sCO2 symposium

List of Tasks

1.1 Project Management and Revisions
1.2 Project Reporting
2.0 Kinetics Data at Low/Medium Pressures
2.1 Ignition Delay Times at Low/Medium Pressures in CH4/O2
2.2 Ignition Delay Measurements at Low/Medium Pressures for Syngas/O2
2.3 Low/Medium Pressure Species Time-histories
3.0 Kinetics Data at High Pressures
3.1 High Pressure Equation of State
3.2 Ignition Delay Times at High Pressures up to 300 bar for CH_4/O_2
3.3 Ignition Delay Times at High Pressures up to 300 bar for Syngas/O_2
3.4 High Pressure species time-histories
4.0 Detailed Chemical Kinetic Mechanism for CH4 combustion
4.1 Adopt a Mechanism for Methane Combustion and Determine Key Reactions
4.2 Update Key Reaction List Using Real Gas Equation of State
4.3 Boxed Molecular Dynamics Simulations
4.4 Mechanism Validation
5.0 sCO2 CFD Development
5.1 Modify OpenFOAM CFD code for real gases, validate with available data
5.2 Implement CMC combustion model to allow very large mechanisms
5.3 Perform design studies of concept burners with CFD

Shock Tube Experimentation

Experiments will be performed in two different shock tube facilities for Methane Oxidation diluted with CO_2 and Argon

Experiments will be performed pressures up to 300 Bar for temperatures between 800 K and 2000 K and equivalence ratios of 0.7 to 1.2

Ignition delay times and key species time histories will be measured

Experiments will also be performed for selected mixtures of syngas

Combustion chemistry

MODEL

Reaction Mechanism Development

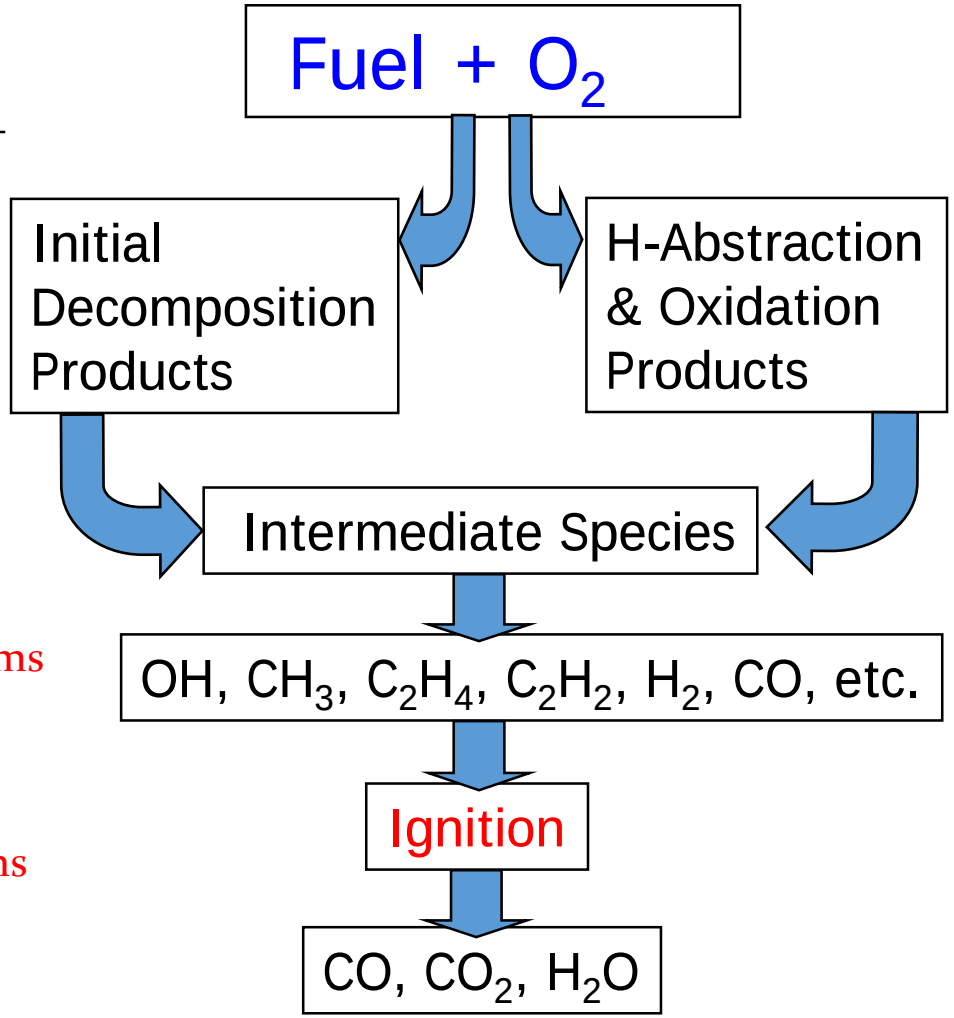
1. Decomposition Pathways

2. Intermediate Species Sub-Mechanisms

3. Full Mechanisms

4. Reduced Mechanisms

5. Validation



EXPERIMENT

Kinetic Targets (Shock Tubes)

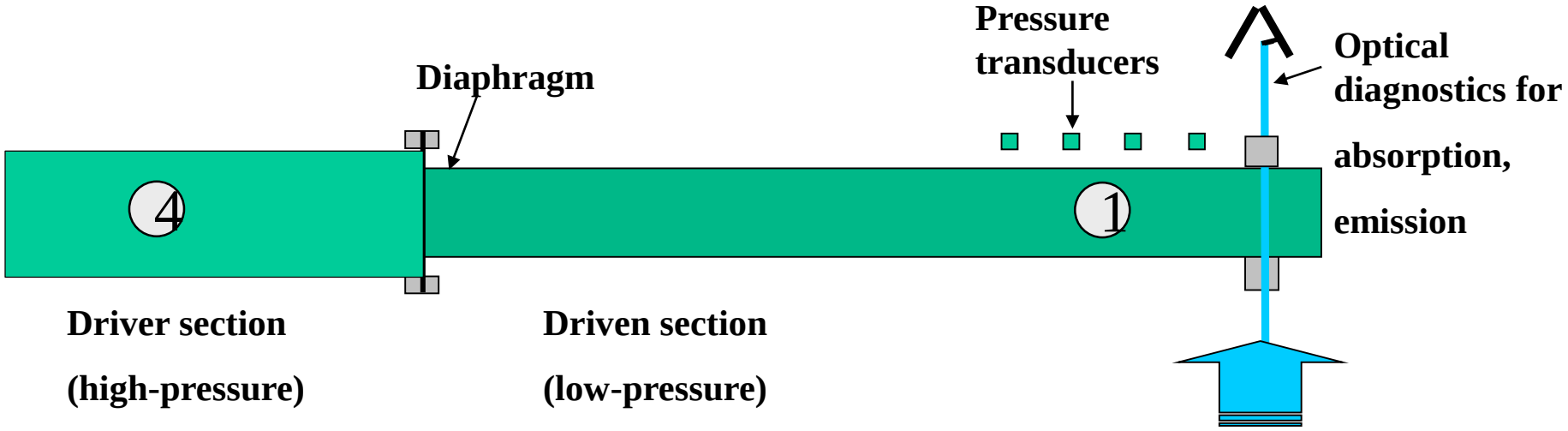
1. Ignition Time Measurements

2. Species Time-Histories

3. Direct Rate Measurements

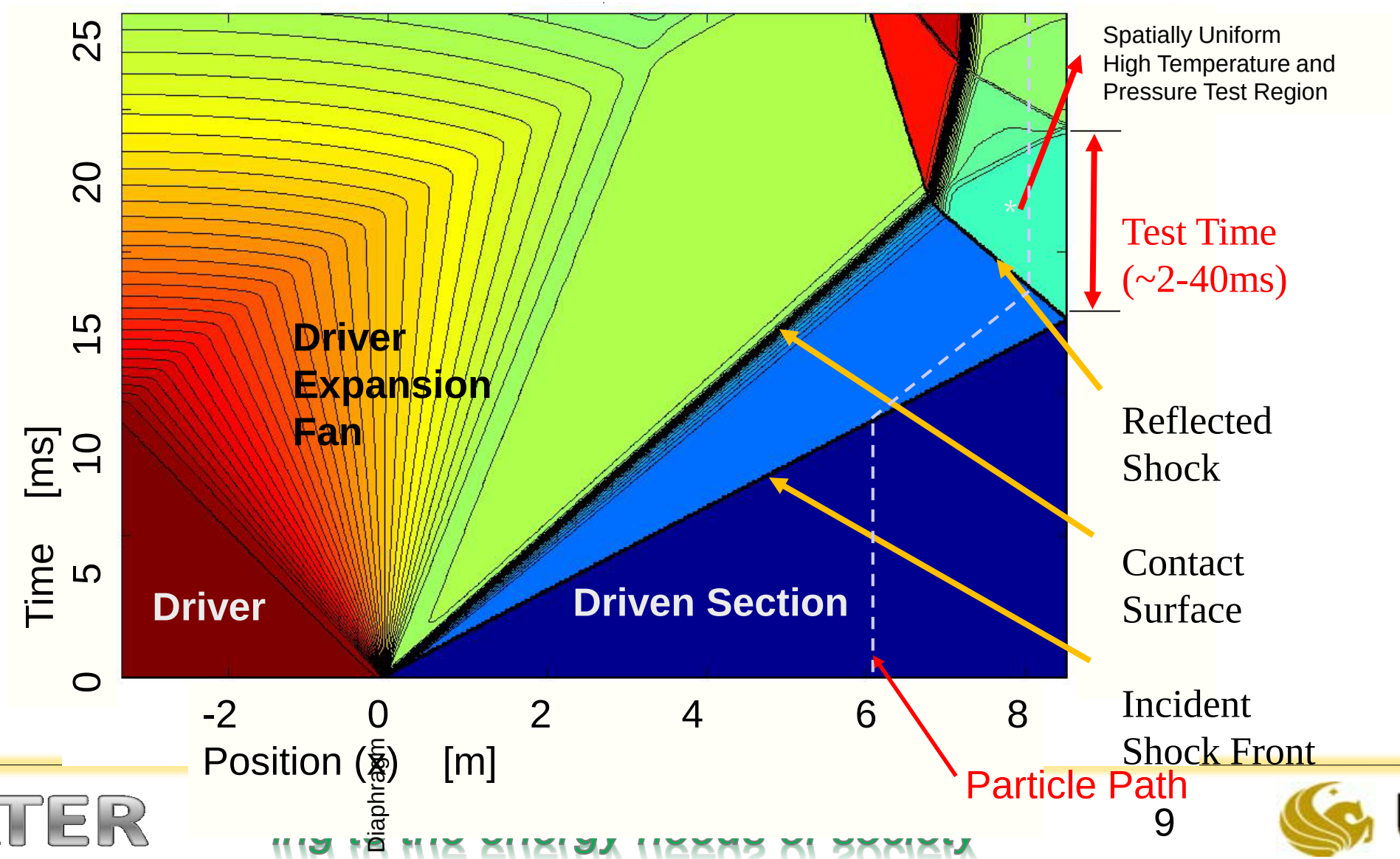
4. Other data from literature

Shock tube operation: Pre-shock filling



- Shock tubes are ideal for studying combustion chemistry
- Step change in T, P and well-defined time zero
- Simple fuel loading
- Accurate mixtures and pre-shock conditions

Shock tube x-t diagram

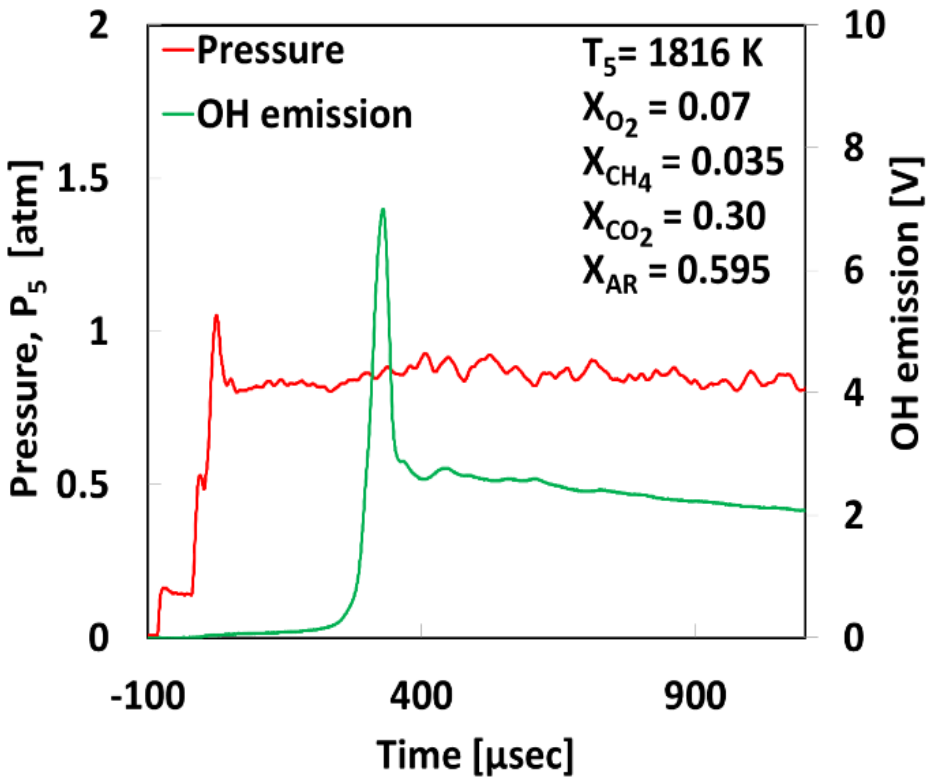


Ignition Delay Time Measurements for Low Pressures

Ignition delay times measured from the arrival of reflected shockwave to rise of the pressure trace

Arrival of shockwave determined as midpoint of the second pressure rise (rise due to reflected shock)

Rise of OH Emissions measured as the intersection between the baseline and the tangent line drawn from maximum rise of OH



Concentrations of Key Species using Laser Absorption

Concentrations of key species will be measured up to the time of ignition

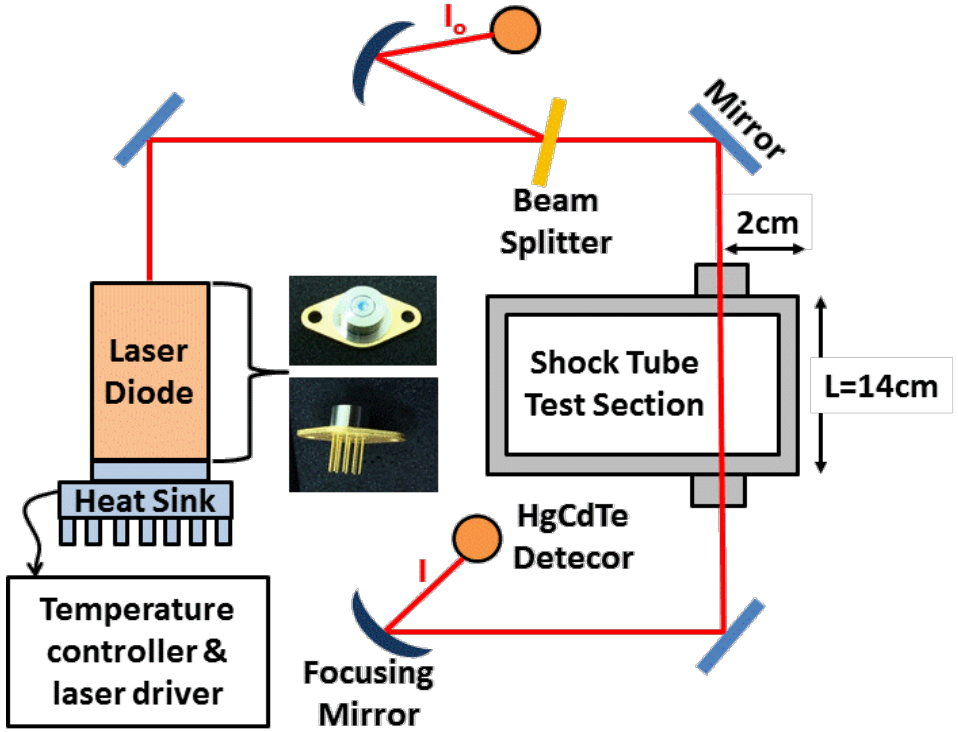
Species time-histories are measured using a peak-valley measurement scheme to remove interfering species

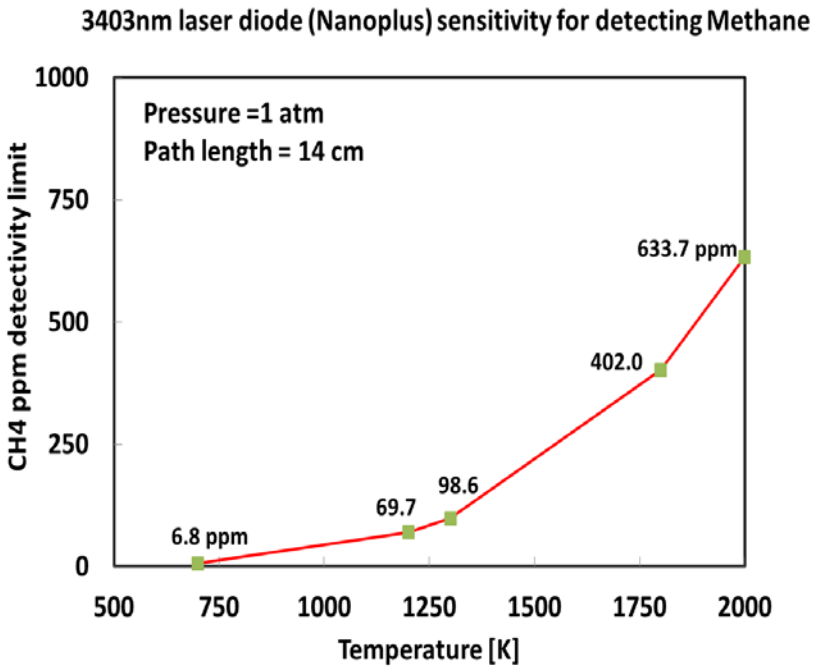
Absorption is measured using the Beer-Lambert law and comparing the intensity of light in the mixture with the intensity under vacuum

$$-\ln\left(\frac{I}{I_o}\right)_\nu = \alpha(\nu,T,P) = S\phi_\nu PL = \beta_\nu PL = \sigma(\nu,T,P)nL$$

$$-\ln\left(\frac{I}{I_o}\right)_\nu = \alpha + \alpha_{\text{interference}} + \tau_{extinction}$$

Methane Sensor Using 3.4um Quantum-Cascade Laser

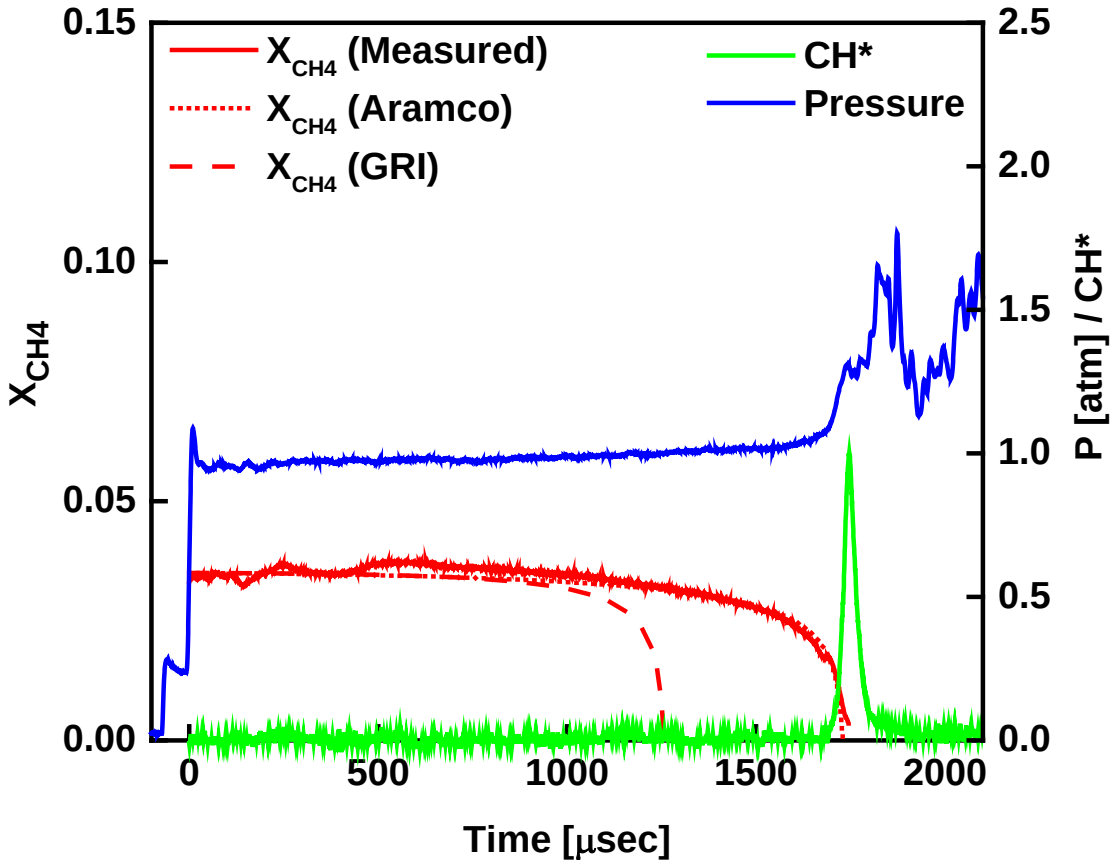




- Methane concentration measurement set up and detectivity showing less than 10 ppm at 800K.
- We have diagnostics for other species (H_2O, CO, CO_2) and Temperature

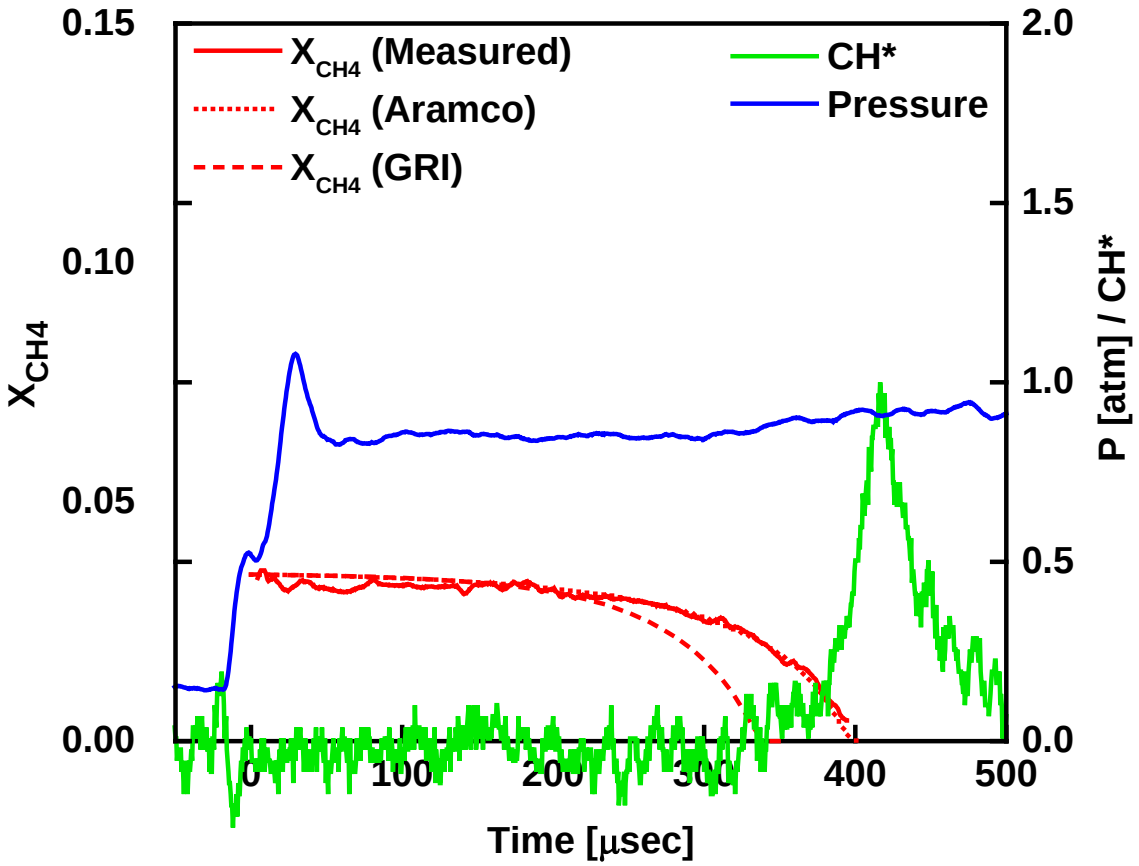
Methane Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH4 in Argon

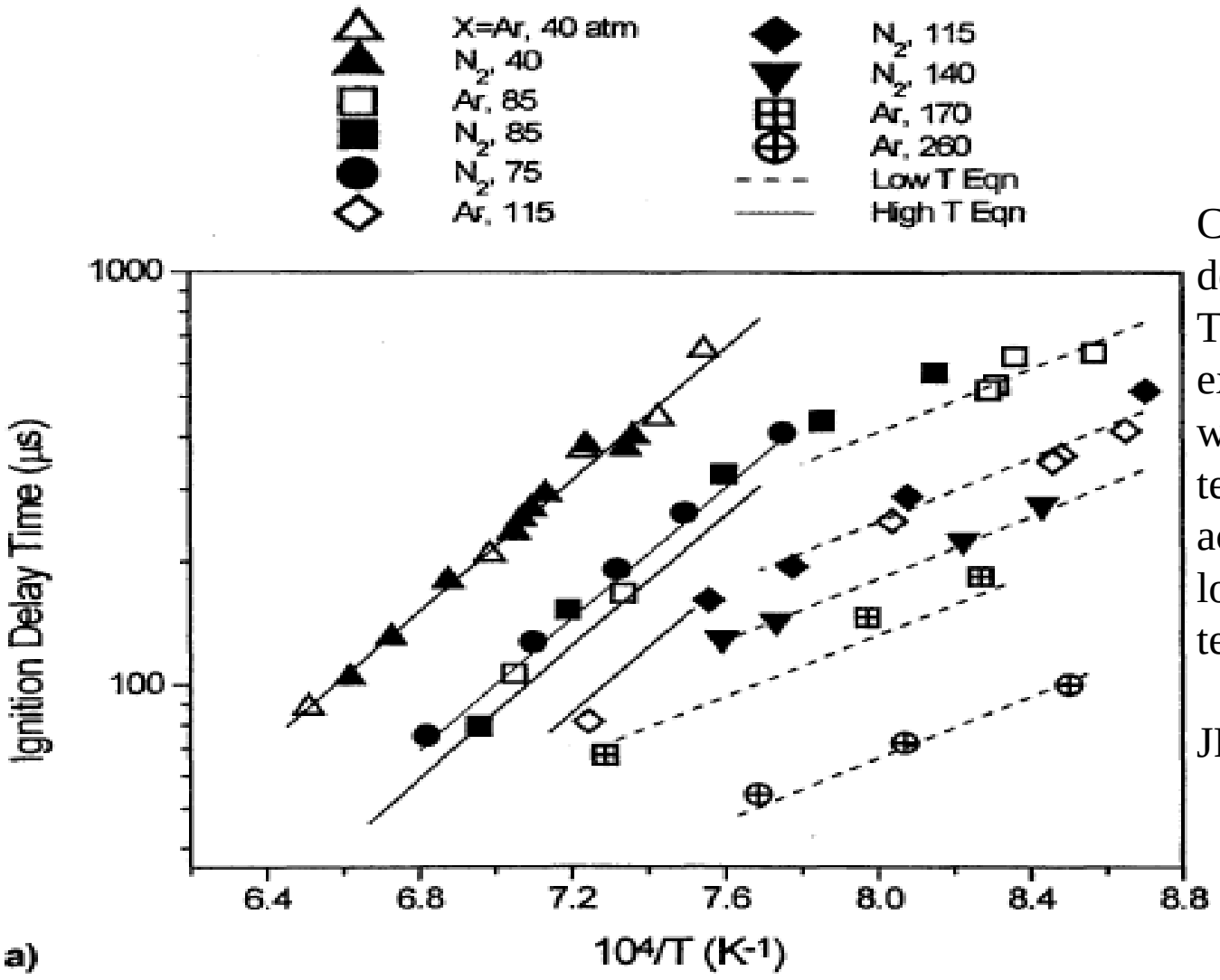


Methane Concentration Results

- Comparison of measured and simulated methane concentration for
  - Stoichiometric ignition of 3.5% CH4 in Argon diluted with 30% CO_2



Existing High-Pressure Methane Ignition Data



$CH_4/O_2/N_2/Ar$ ignition delay time measurements. The higher pressure data exhibit a significantly weaker variation with temperature (smaller activation energy) than the lower pressure, higher temperature mixtures

JPP, 1999, 15(1), 82-91

Chemical Kinetic Mechanism Summary

- Combustion Kinetics of c_0-C_6 hydrocarbons includes 1161 species and 5622 elementary reactions (RD2010)

- Existing kinetic models are only valid at low pressures

- We will use multiscale modeling approach to extend their validity to above 300 bar by:

  1. Quantum Mechanic simulations of the activation enthalpies in gas vs. CO_2 environment

  2. Boxed Molecular Dynamic simulations of reaction processes

The important elementary steps in RD2010 mechanism of C0-C4 fuel combustion

Table 4 Important reactions and the source of their rate constants used in the mechanism. Rate coefficients are in units of cal, mol, cm^3, K. Rate constants are calculated as $k = A*T^n*Exp(-Ea/RT)$ where T represents temperature and R represents the gas constant.

No.	Reaction	A	n	Ea	Ref.
1	$H+O_2=O+OH$	3.55E+15	−0.406	1.66E+04	[7]
2[c]	$CO+OH=CO_2+H$	2.20E+05	1.89	−1.16E+03	[7], A*1.24
3	$HCO+M=H+CO+M$	4.75E+11	0.7	1.49E+04	[6][a]
4	$H+OH+M=H_2O+M$	4.50E+22	−2	0.00E+00	[19][a]
5	$C_3H_5\text{-a}+H(+M)=C_3H_6(+M)$	2.00E+14	0	0.00E+00	[8]
	Low pressure limit:	1.33E+60	−12	5.97E+03	
	Troe parameters: 0.02, 1.10E+03, 1.10E+03, 6.86E+03				
6	$CH_3+CH_3(+M)=C_2H_6(+M)$	9.21E+16	−1.17	6.36E+02	[7][a]
	Low pressure limit:	1.14E+36	−5.246	1.71E+03	
	Troe parameters: 0.405, 1.12E+03, 69.6, 1.00E+10				
7	$CH_3+HO_2=CH_3O+OH$	1.00E+12	0.269	−6.88E+02	[7]
8	$CH_4+H=CH_3+H_2$	6.14E+05	2.5	9.59E+03	[7]
9	$HO_2+HO_2=H_2O_2+O_2$	4.20E+14	0	1.20E+04	[18][b]
		1.30E+11	0	−1.63E+03	
10	$CH_4+HO_2=CH_3+H_2O_2$	1.13E+01	3.74	2.10E+04	[7]
11	$CH_3O_2+CH_3=CH_3O+CH_3O$	5.08E+12	0	−1.41E+03	[7]
12	$CH_3+OH=CH_2(S)+H_2O$	4.51E+17	−1.34	1.42E+03	[7]
13	$CH_3+O_2=CH_2O+OH$	2.64E+00	3.283	8.11E+03	[7]
14	$CH_3+H(+M)=CH_4(+M)$	2.14E+15	−0.4	0.00E+00	[1][a]
	Low pressure limit:	3.31E+30	−4	2.11E+03	
	Troe parameters: 0.0, 1.00E-15, 1.00E-15, 40.0				
15[c]	$C_2H_4+H(+M)=C_2H_5(+M)$	1.95E+12	0.454	1.82E+03	[7][a], A*1.8
	Low pressure limit:	2.16E+42	−7.62	6.97E+03	
	Troe parameters: 0.975, 210, 984, 4.37E+03				

[a]Collision efficiencies: CH_4 2.0, CO 1.9, CO_2 3.8, C_2H_6 3.0, H_2O 6.0, H_2 2.0, Ar 0.7.
[b]Rate constant is the sum of two expressions.
[c]c.f. text.

C.V. Naik, K.V. Puduppakkam, E. Meeks, *J Eng Gas Turbines Power* **2012**, 134, 021504.

Quantum Chemical calculations in the framework of Transition State Theory (TST)

Experimental rate constant is often analyzed in terms of modified Arrhenius equation:

$$k = A*T^{n}*Exp(-Ea/RT)$$

According to transition state theory (TST), the bimolecular reaction A+B→C is approximately considered as a two-step process:

A..B ↔TS→C

Here the transition state (TS, a.k.a. activated complex $AB^{\neq}$) is formed in a reversible step and coexists in thermal equilibrium (as governed by Boltzmann statistics) with the reaction complex A..B, and is converting to the product C irreversibly. Quantum Chemical methods are then used to obtain the enthalpy and entropy of the activated complex: $\Delta H^{\neq}$ and $\Delta S^{\neq}$:

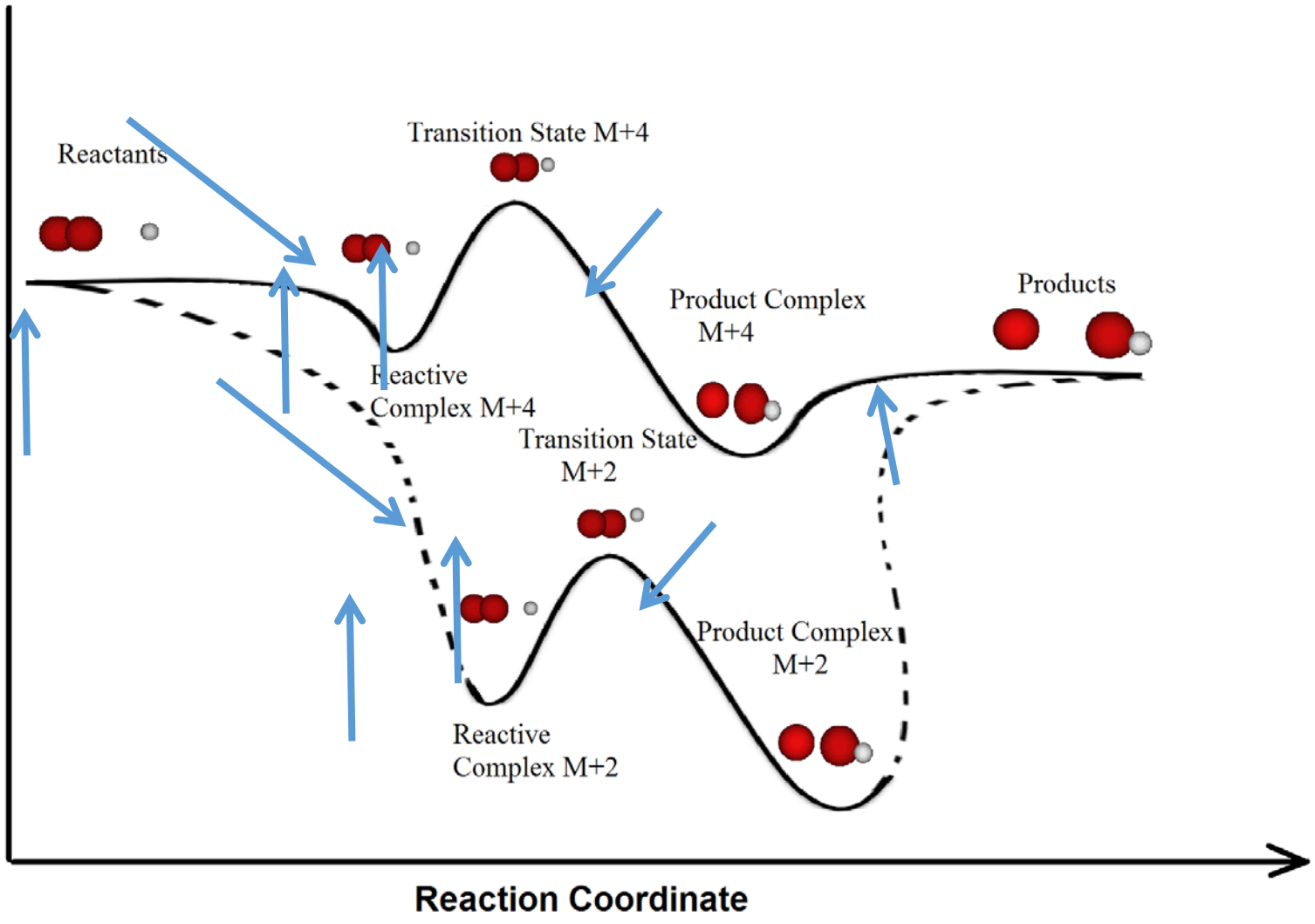
$$k = \frac{k_B T}{h} e^{-\Delta H^{o,\ddagger}/RT} e^{\Delta S^{o,\ddagger}/R}$$

The $\Delta H^{\neq}$ is then approximately corresponds to $\boldsymbol{E_a}$ from Arrhenius equation; $\Delta H^{\neq}$ is always positive. Zero $\Delta H^{\neq}$ values require free energy potential surface, as described by Variational TST (VTST). Negative values of $\boldsymbol{E_a}$ can be observed as a result of decreased equilibrium concentration of A..B at higher temperatures prior to TS formation:

A+B ↔ A..B

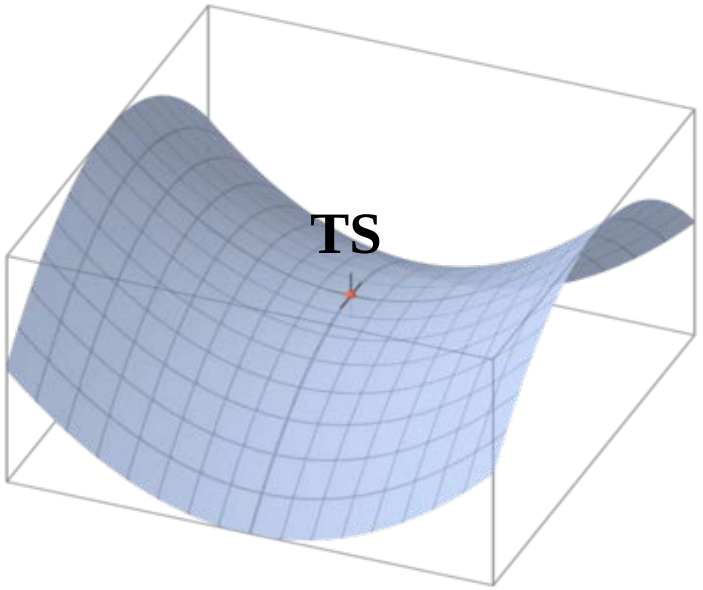
Elementary Reaction O2+H→O+OH

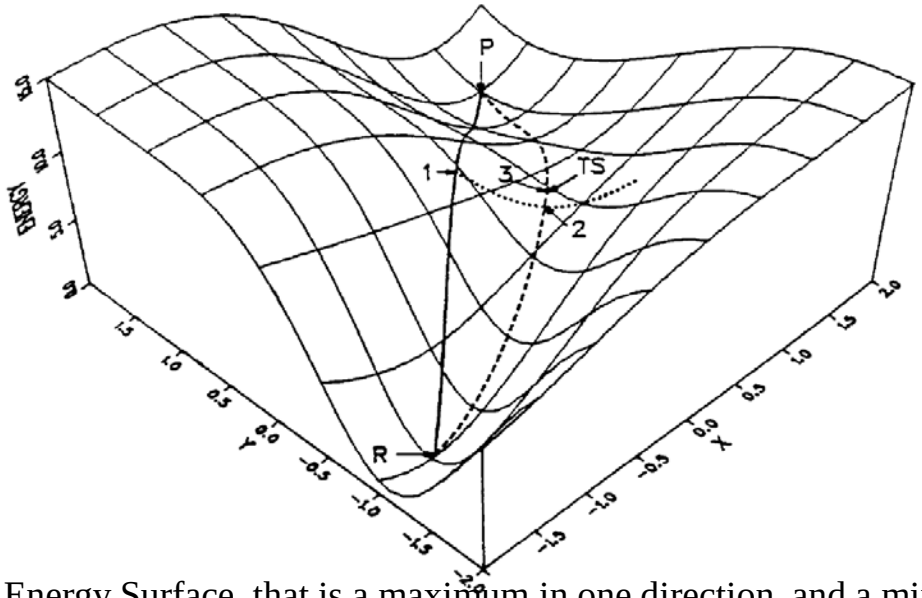
- Five distinct steps along Reaction Coordinate:
  1. Reactants (R1,R2)
  2. Reactive complex (RC)
  3. Transition state (TS)
  4. Product complex (PC)
  5. Products (P1,P2)
- Two radicals may couple high spin or low spin; these result in two reaction surfaces with two different multiplicities
- QST3 method will be used to locate Transition state
- IRC method will be used to confirm Transition state



Synchronous Transit-guided Quasi-Newton method is used to locate TS structure

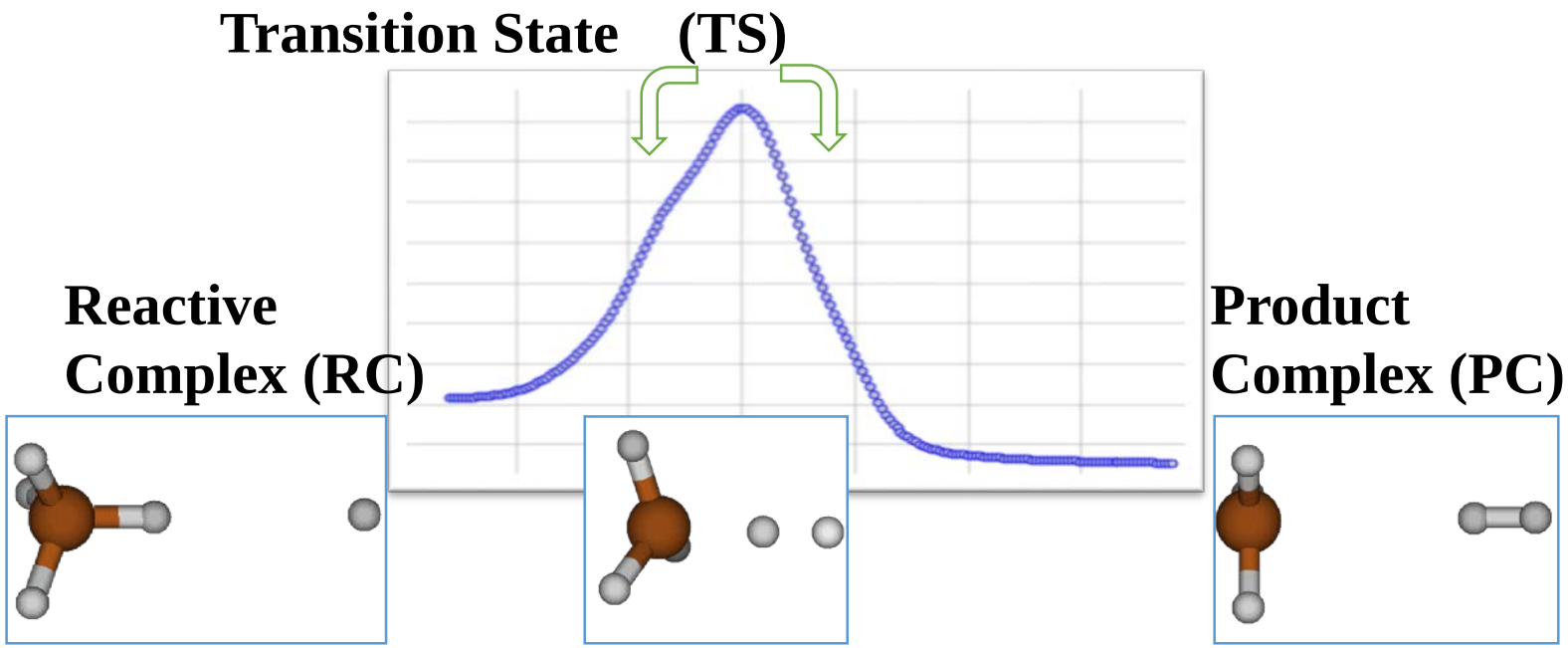
- **QST2**: input a reactant-like structure and a product-like structure
  QST3: input reactant, product, and estimate of transition state





- TS is the first order saddle point on Potential Energy Surface, that is a maximum in one direction, and a minimum in all other directions.
- In order to find the structures of the transition states we use the Synchronous Transit-guided Quasi-Newton method implemented in Gaussian09 via one of the two keywords: QST2 (coordinates for the reagents and products are needed as input) or QST3 (where coordinates for the TS structure guess is needed also).

Intrinsic Reaction Coordinate method verifies that located TS is connected to particular RC, PC



In order to verify the nature of the located TS, the Hessian needs to display one negative eigenvalues. Aside from this local criterion, it is also necessary to identify the minima connected through the transition state. This is performed through calculation of the intrinsic reaction coordinate (IRC), defined as the minimum energy reaction pathway (MERP) in mass-weighted Cartesian coordinates between the transition state of a reaction and its reactants and products. It is the path from the activated complex down the product and reactant valleys with zero kinetic energy. The Gonzalez-Schlegel method, implemented in Gaussian09, is evoked using the IRC keyword.

Effects of supercritical solvent within framework of Transition State Theory

The supercritical solvent can modify predictions of this model in three ways:

1. changing the ability to reach the equilibrium by the reactants and/or TS
2. shifting this equilibrium, and
3. changing probability of TS to convert to the products

1. Reaching the equilibrium between reactants and TS may be limited by diffusion

Noyes theory expresses the reciprocal observed rate constant k as the sum of the reciprocal diffusion rate constant k_d and the reciprocal activation rate constant k_r:

$$\frac{1}{k} = \frac{1}{k_d} + \frac{1}{k_r}$$

The reaction is diffusion controlled when $k_d >> k_r$. This means that diffusion of the reactants A and B until they approach reactive distance R_{AB} is the rate limiting step. This diffusion rate constant is expressed by the Smoluchowski equation:

$$k_d = 4\pi N (D_A + D_B) R_{AB} \beta_{spin}$$

where N is Avogadro's number, D_A and D_B are diffusion coefficients, and β_{spin} is the spin factor. A random encounter between two radicals can produce a reactive singlet with spin factor of 0.25. However, the triplet radical pair that do not react at their first encounter have a finite probability to re-encounter before diffusing out of the solvent cavity. Their spin relaxation to the singlet state occurring within a reencounter time could elevate β_{spin} above 0.25, and further increase it with the lifetime of nonbonded A..B complex. **The diffusion coefficient for each reactant will be calculated by Molecular Dynamics (MD) methods (while the reactive distance R_{AB} and Force Field parameters for use in MD will be obtained from Quantum Chemical calculations)**.

2. Shifting the equilibrium between reactants and TS can be affected by two factors

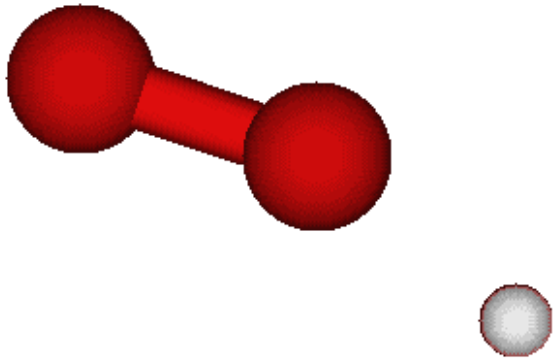
Both factors will be studied using Quantum Chemistry methods:

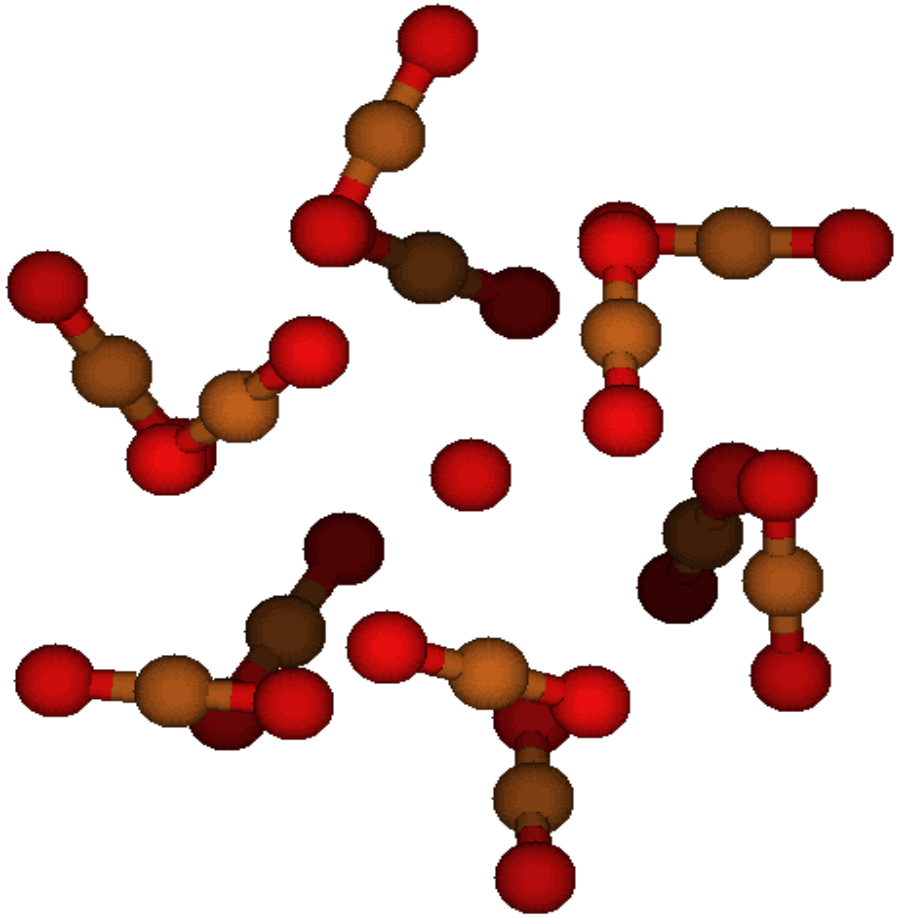
- Changing reaction mechanism (CO_2 may be involved in TS structure)

- Products and TS may be stabilized by CO_2 to a different degree (thus, changing $\Delta H^{\neq}$)

Effect of CO_2 environment will be simulated by $(CO_2)_{12}$ cluster

- Global optimization of 13 CO_2 molecules at PM6-D2 theory level produced the cluster, simulating solvation shell
- We will replace the central CO_2 molecule with TS





3. Changing probability of TS to convert to the products needs Molecular Dynamics

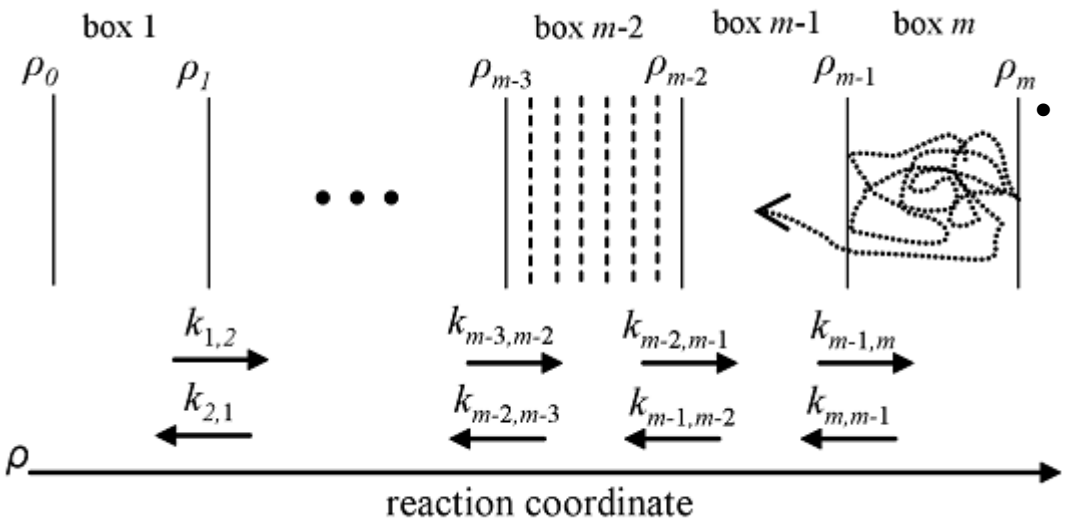
One of the assumptions of TST is that the trajectories that arrive at the barrier top with velocities directed towards the product state will end in the product state: re-crossings of the free energy barrier are neglected. For reactions in supercritical fluid phase, this assumption may break down and the re-crossing corrections may change the value of the TST estimate. Specifically, encounter with the solvent cage can backward scatter the product trajectory over TS region and into the reactant basin.

This mechanism and other deviations from TST predictions will be studied with Molecular Dynamics simulations.

Crossing the activation barrier is infrequent event. Therefore, accelerated MD protocols must be used for efficient use of CPU time. We will employ Boxed MD method, as implemented in CHARMM

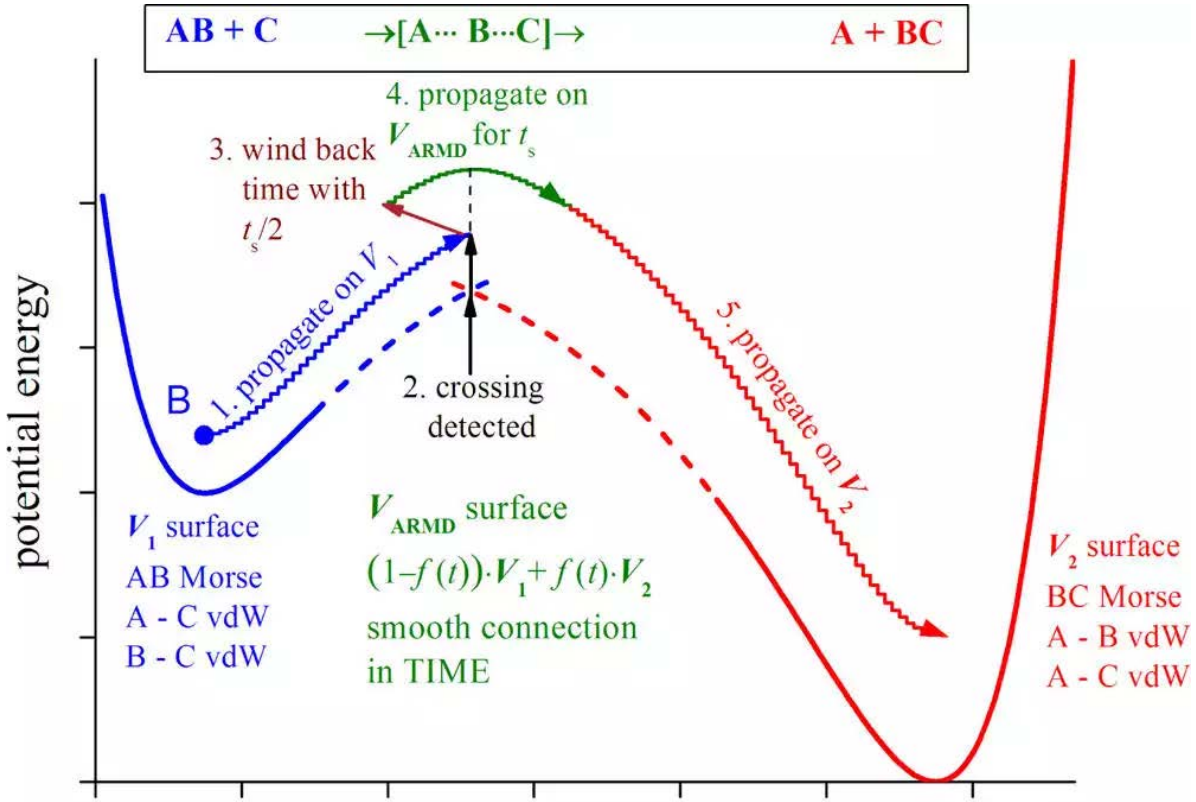
Boxed Molecular Dynamics (BXD) is a multiscale technique to study infrequent events

- BXD splits the reaction coordinate into several boxes and subsequently lock the dynamics in each box by inverting the velocity of the trajectory in the direction of the reaction coordinate every time the trajectory hits a boundary between two adjacent boxes. Then rate constant of exchange between the boxes is calculated as inversed average time between the ‘hits’.



- A set of kinetic rate constants of exchange between the boxes can be used to recover free energy profile.
- Longer time-scale dynamics may be calculated from the set of rate constants obtained from short-time simulations within each box. This connection between short and long time scales is what makes BXD a multiscale method.

Empirical Force Field treatment: Multi-Surface Adiabatic Reactive MD (MS-ARMD)



- MS-ARMD algorithm is schematically shown for collinear atom transfer reaction (AB+C=A+BC). During the crossing, the reactant and product surfaces are mixed smoothly. These surfaces differ in that the Morse bond is replaced by van der Waals (vdW) interactions and vice versa.

T. Nagy, J. Yosa and M. Meuwly, *J. Chem. Theory Comput.*, **2014**, 10, 1366–1375

OpenFOAM CFD Program

- OpenFOAM is an open source CFD code written in c++.
- Provides a wide range of sub-models, easily modifiable.
- Will use the premixed CMC turbulent combustion model added by Velez & Martin.
- Will add the non-premixed CMC turbulent combustion model.
- Modify CMC equations for real gases.
- Modify energy and turbulence equations for real gases.

Equation of State

- Will investigate several real gas equations of state such as REFPROP from NIST.
- Use existing data for validation.
- Modify the energy, turbulence and CMC equations for non-ideal gases.

Thermodynamic Data

- Use existing real gas thermodynamic data for enthalpy, specific heat, thermal conductivity, Lewis number, Prandtl number, incorporate into OpenFOAM.

Kinetic Mechanism

- Initial CFD work will be done with an existing detailed sCO2 kinetic mechanism.
- Explore how the Arrhenius reaction rate expressions must be modified for real gases.
- Use shock tube data obtained in this work to improve the kinetic mechanism.
- Implement into the CMC code.

OpenFOAM Enhancements

- A number of OpenFOAM enhancements will be performed;
  - Shape of the joint PDF.
  - Functional form of the variance equation for the reaction progress variable and mixture fraction.
  - Shape of the scalar dissipation for the reaction progress variable and mixture fraction.
  - Should the conditional velocity term be added to the premixed CMC equation.

Concept Burner Studies

- Perform sensitivity studies of the sub-models and their model assumptions.
- Perform sensitivity studies of concept burner design parameters.
- Model available sCO2 cycles to validate the new CFD code.
- Perform design optimization for the recommended sCO2 cycle.

Thank you,
Questions?