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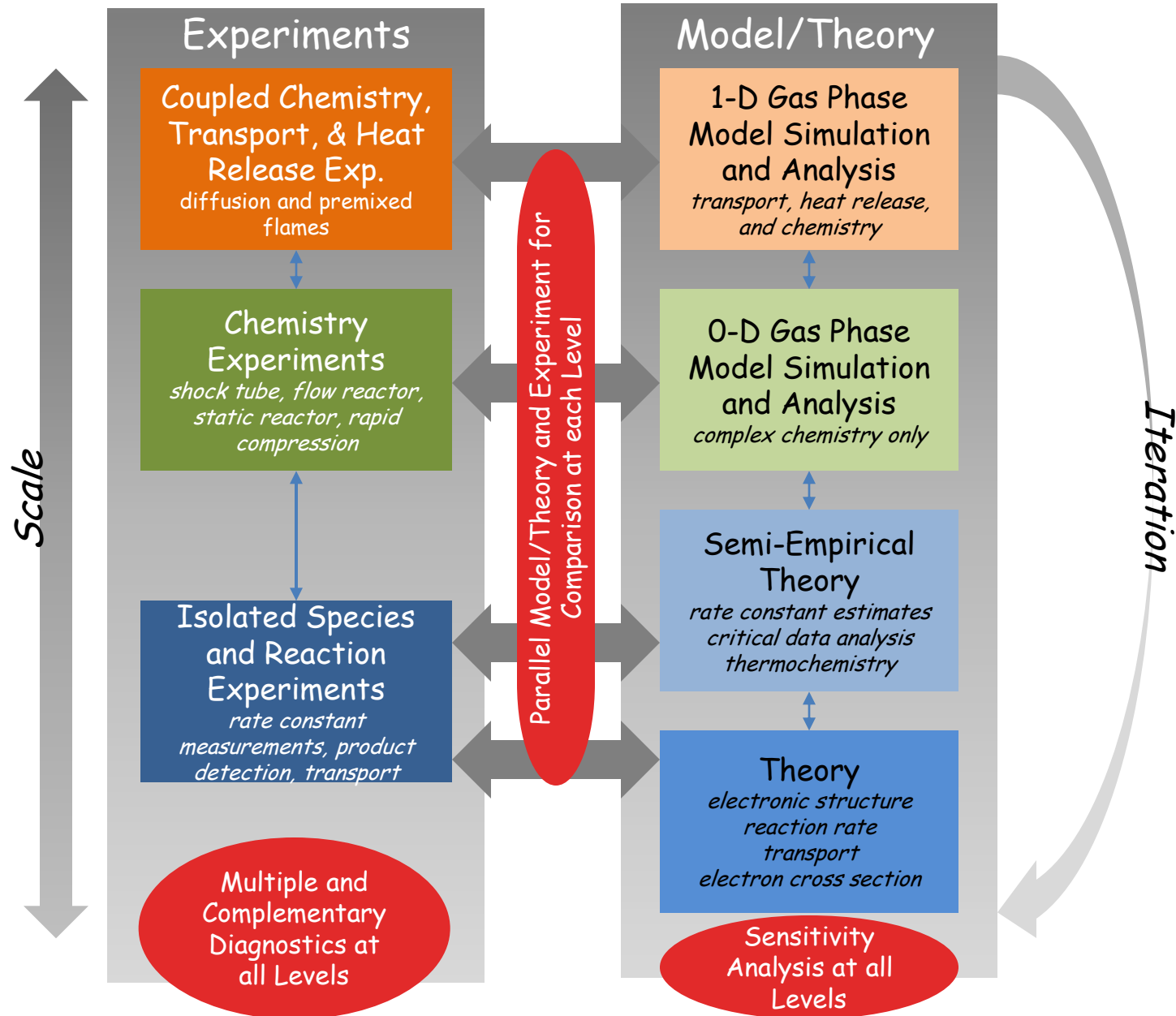
# AFOSR PAC Kinetics Roadmap

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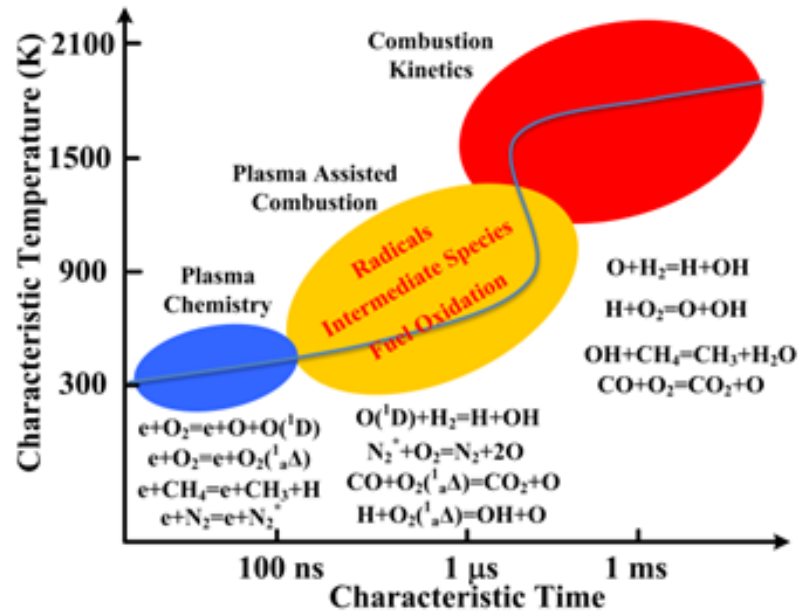
# Plasma Assisted Combustion Chemistry Model Development



# Three timescale experiments

1. 10-1000 ns, Plasma chemistry: electron impact excitation and energy transfer in fuel/air mixtures

Using short pulse laser to detect excited (electronic & vibrational) species and radical production.



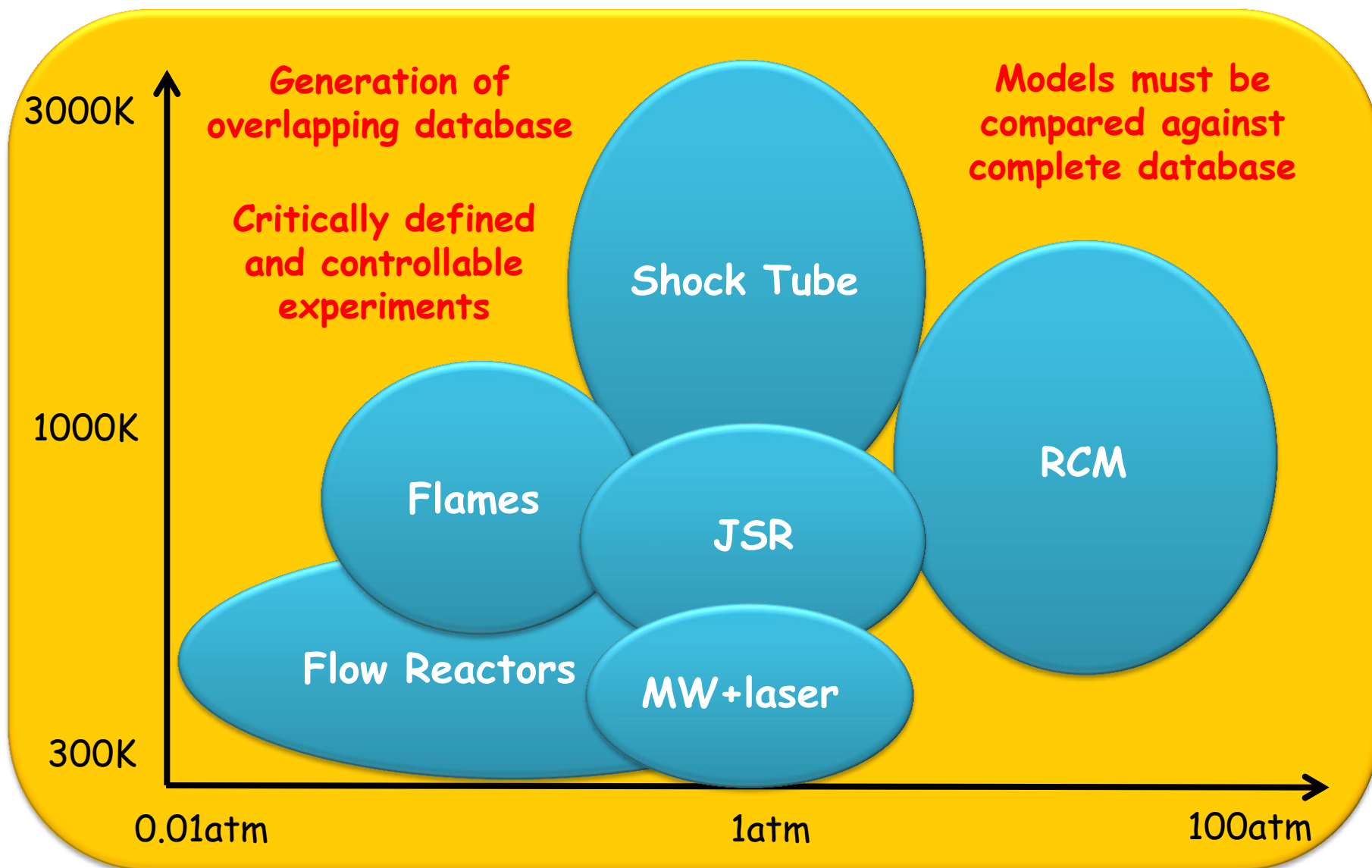
2. 1 μs-10 ms, Plasma assisted low temperature energy relaxation and chemistry.

Quantification of fuel oxidation and intermediate species production via interaction between plasma generated long lifetime excited species and reactants at low temperature. Using short pulse plasma and conducting species time history diagnostics.

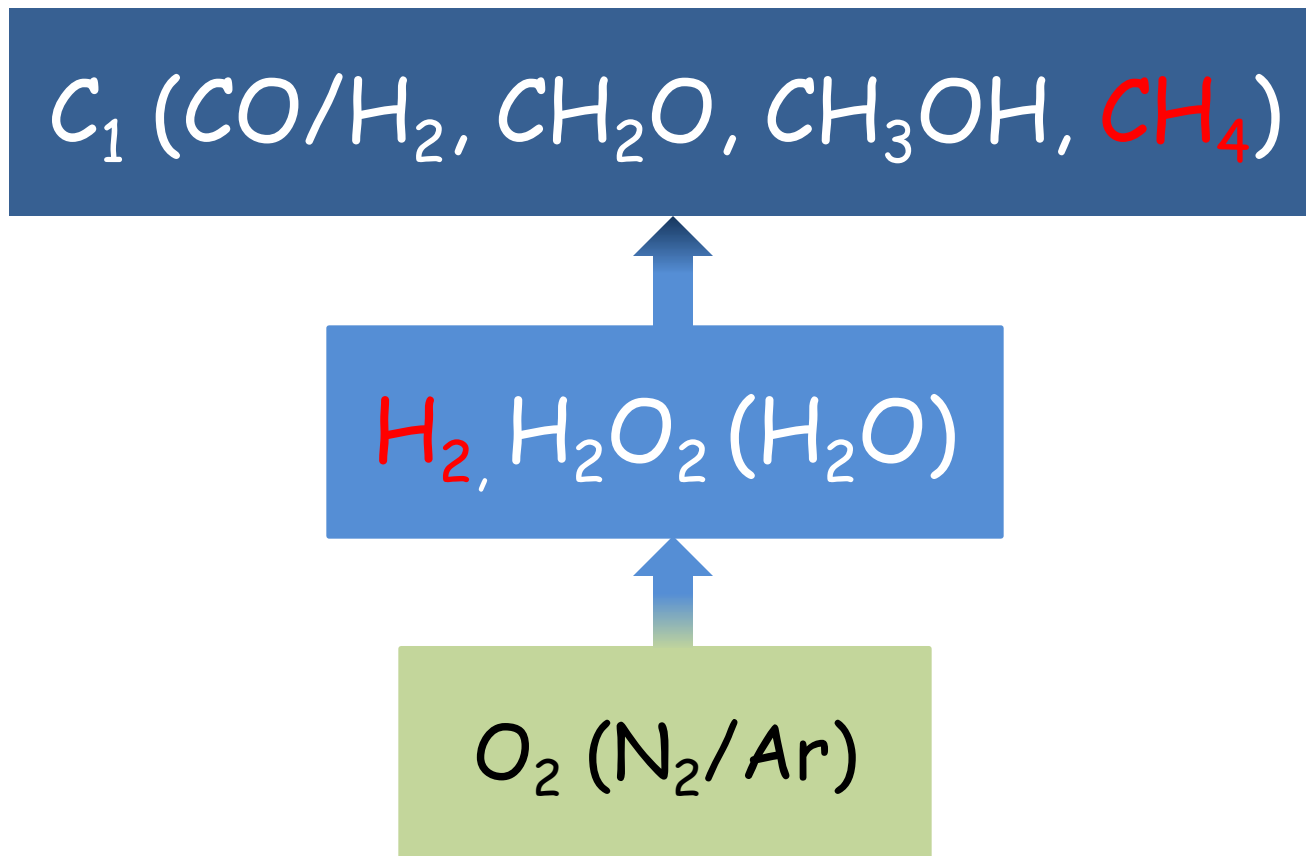
3. 1 ms-1 s, Low temperature combustion kinetics with plasma activation

Kinetic measurements of the global impact of plasma discharge on ignition, fuel oxidation, and low temperature combustion.

# Kinetic Data Generation



# Hierarchical Fuel Mechanism Analysis



# PAC Kinetics Roadmap - Challenges

- *Low temperature chemistry of fuel air mixtures below the conditions of autoignition poorly known- extrapolation of high temperature mechanisms to low temperatures insufficient*
- *Uncertainties in reaction branching ratios, rate constants, products for reactions with electronically and vibrationally excited species, and potential energy surfaces during collision process*
- *Gas discharge homogeneity/inhomogeneity*

# Questions Addressed

- What are the observables that can be measured?
- What are the measurement techniques?
- What are the experimental parameters needed for accurate model analysis?
- What are the gaps?

# What are the observables that can be measured?

- Intermediate Species
  - O, H, OH
  - HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>
  - Depending on the fuel: HCO, CH<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>, R (most difficult)
- Major Species (Fuel, Intermediate, Product)
  - RH, R'H, H<sub>2</sub>, CH<sub>2</sub>O, H<sub>2</sub>O, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>
  - Depending on the fuel: Peroxides, Aldehydes, Ketones, Ethers (most difficult)
- Excited Species
  - N<sub>2</sub><sup>\*</sup>(A,B,C), N<sub>2</sub>(X,v), O(1D), O<sub>2</sub>(1Sigma), O(1D) (indirect meas.)
- Desirable to track at least one species from each of the above groups, difficult time dependent measurements



# What are the measurement techniques?

- In-situ techniques
  - CARS (T, T<sub>v</sub> and vib. level populations of N<sub>2</sub>)
  - LIF (OH, CH<sub>2</sub>O, NO), TALIF (O, H, N)
  - 4-wave mixing (electric field)
  - Thomson scattering (electron density)
  - Absorption spectroscopy (T, OH, CO, CH<sub>2</sub>O, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>)
  - Faraday rotational spectroscopy (OH, HO<sub>2</sub>, O<sub>2</sub>)
  - Emission spectroscopy (CO, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>, H<sub>2</sub>O, N<sub>2</sub><sup>\*</sup>, CO-O)
  - Radar REMPI (O, O<sup>\*</sup>, H, H<sup>\*</sup>, OH, N<sub>2</sub><sup>\*</sup>, O<sub>2</sub><sup>\*</sup>, CH, CO)
- Extraction techniques
  - FTIR (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> fuels, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>2</sub>O, NO<sub>x</sub>)
  - GC/MS (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>1</sub>-C<sub>x</sub> hydrocarbons, many oxygenates)
  - Molecular Beam (HCO, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>, H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O)

# What are the Gaps?

- Adequate description of the plasma: geometry, 2-D, 3-D effects, local and non-local descriptions;
- Cross-sections for hydrocarbons excitation by electron impact;
- Quenching of excited states of nitrogen and oxygen by hydrogen and hydrocarbons - rates and products;
- Ionic chains - ion reactions with hydrocarbons - rates and products;
- Vibrational chains - reactions of vibrationally-excited molecules and radicals; vibrational energy transfer;
- Electronic excitation - reactions of electronically-excited molecules and radicals - rates and products;
- UV decomposition of hydrocarbons and Peroxides, Aldehydes, Ketones, Ethers... - products;
- Mechanisms of plasma recombination - products and rates of energy release;
- Possible coupling among different energy modes, synergetic effects of different types of excitation;

# What are the Gaps - continued?

- Low temperature chemistry (300-700 K);
- Time dependent measurements of excited and intermediate species.

# PAC Kinetics H2 Model Development

## Plasma model:

- Plasma assisted combustion models for hydrogen oxidation understood for conditions of low energy loading per molecule. It means low ionization degree - we can neglect e-e collisions and EEDF Maxwellization due to this process.
- We have complete set of cross-sections for rotational, vibrational and electronic excitation, dissociation, dissociative ionization, ionization. These cross-sections were verified both for two-term approximation of Boltzmann equation (local EEDF) and could be modified for non-local case of extremely strong electric fields (differential cross-sections are also available).

## Afterglow Model:

- Because of fast relaxation we assume  $T_{tr} = T_{rot}$  for ground state.
- We have recombination rates for ion-electron collisions, ion-ion recombination (in some cases the products are unknown). Rates of complex ions formation/decomposition are unknown for elevated temperatures - but these ions control the plasma recombination rate.
- Quenching rates of major states are available, in some cases products are unknown. Specifically we do not know the products of reactions  $N_2^* + H_2 \rightarrow \dots$

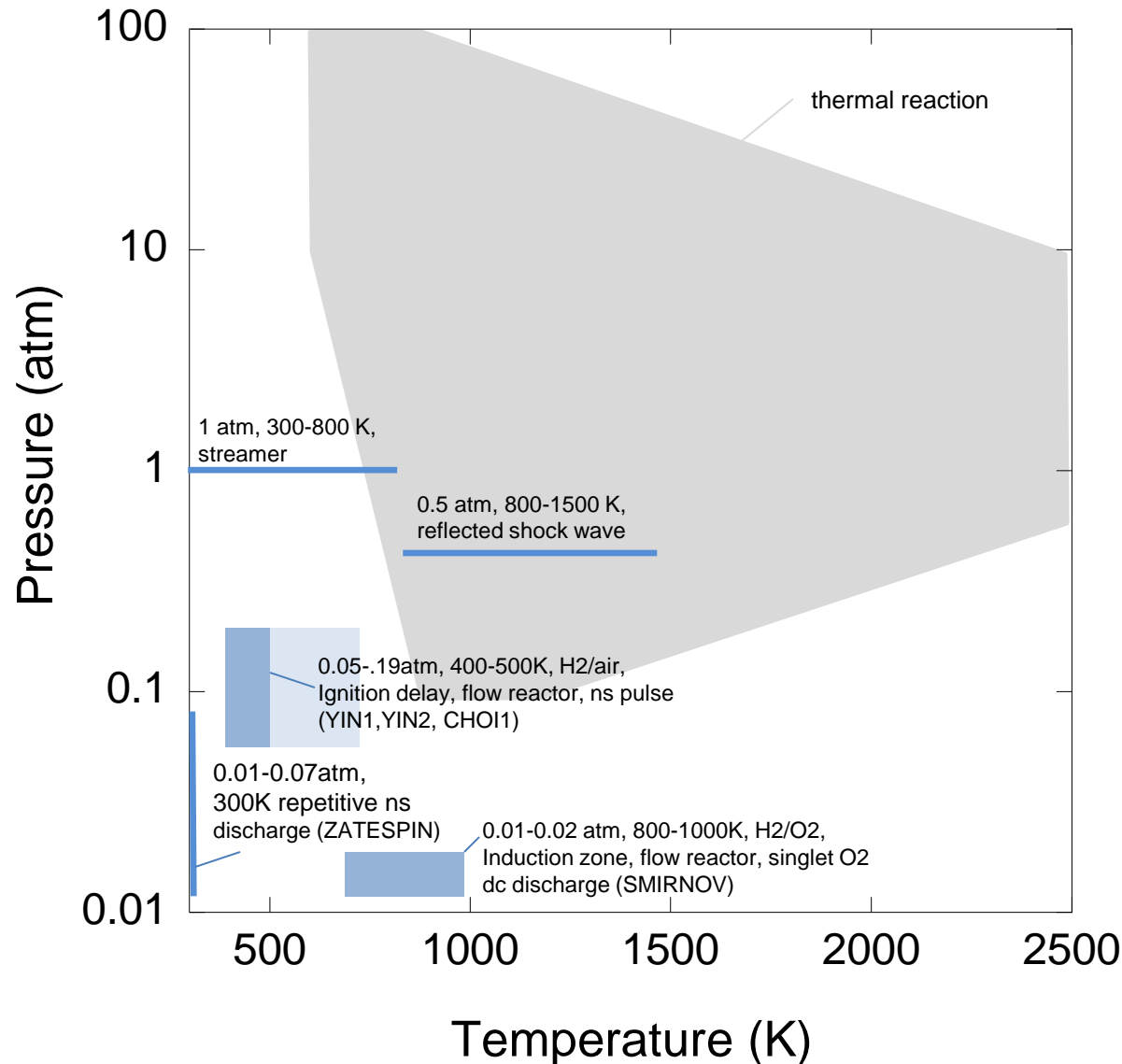
## Chemical Model:

- We have complete state-to-state model of chemical reactions including vibrationally-nonequilibrium conditions for H<sub>2</sub>-air system since 2001.
- We have verified this model for 300 K (low-P reactor), 300-800 K (1 atm streamer) and 800-1500 K (0.5 atm, reflected shock wave).

## Unsolved problems:

- Because of huge number of reactions some pathways are still questionable. We need to investigate in more details the products of electron-ion and ion-ion recombination, products of electronic states dissociative quenching (focus on electronically-excited products formation).
- Reaction rate coefficients of electronically and vibrationally excited species should be verified in some cases.
- We need additional analysis of the role of complex ions in recombination and chemistry at low-T conditions.

# Regions of Comparison between Experiment and Model for H<sub>2</sub>/O<sub>2</sub> Chemistry



# H<sub>2</sub>/O<sub>2</sub> Database

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# Extra Slides

# Plasma Assisted Combustion Chemistry

## General Approach

- Identify the important species and states and determine their associated thermochemical parameters and corresponding uncertainties.
- Identify the important reactions and determine their associated rate parameters and corresponding uncertainties.
- Calculate the time and spatial dependent solutions of species and temperature profiles and associated sensitivities.
- Measure or calculate (using fundamental theoretical methods) parameters that have simultaneously large sensitivities and large uncertainties.
- Design experiments for both parameter measurement and systems validation.
- Perform model and experiment comparisons
- Iterate through the above steps.



# What are the experimental parameters needed for accurate model analysis?

- *Complete definition:* pressure, initial species concentrations, temperature, velocity, electric field in plasma, and electron concentration (to provide how much energy goes in ( $E$ ,  $n_e$ ), its partition among internal energy modes ( $E/N$ ), and what net fraction of it goes to heat ( $T$ )), current and voltage shapes, discharge uniformity, flow residence time, boundary conditions.
- *Satisfactory definition:* pressure, initial concentrations, energy input, temperature, dynamics and spatial distribution of energy input, and electrical field.

## **Experiments: two parallel thrusts (current – 2014)**

**1.1.** Low-T chemistry of "conventional" (non-excited) species: energy addition to plasma on time scales greater than excited species relaxation / quenching time. Use of large volume (e.g. plane-to-plane), repetitively pulsed plasmas. **H<sub>2</sub>-air, CH<sub>4</sub>-air, species and T vs. time**

**1.2.** Reactions involving excited species (vibrational and electronic): energy addition to plasma on time scales shorter than excited species relaxation / quenching time. Use of small volume (e.g. pin-to-pin), single-pulse plasmas. **H<sub>2</sub>-air, CH<sub>4</sub>-air, species, T, and T<sub>v</sub> vs. time**

## **Modeling: two thrusts, serial or parallel\***

**2.1.** "Conventional" low-T chemistry mechanism: identifying "critical" species and reaction pathways. Rates accuracy / availability assessment. 0-D parametric sensitivity analysis over a range of T, P, and  $\phi$ . **H<sub>2</sub>-air, CH<sub>4</sub>-air . Time frame: current**

**2.2.** Effect of excited and charged species reactions: coupling SOTA air-fuel plasma model with SOTA low-T conventional chemistry model, identifying "critical" species and reaction pathways. Rates accuracy / availability assessment. 0-D parametric sensitivity studies over a range of  $n_e/N$ ,  $E/N$ , T, P, and  $\phi$ . **Time frame: current (H<sub>2</sub>-air), current – 2014 (CH<sub>4</sub>-air).**

## **\*Benefit of serial thrusts in modeling**

Low-T rates for reactions of excited species, such as  $N_2(^1X, v) + O \rightarrow NO(^2\Pi, w) + N$ , are uncertain at best, or unavailable. Early focus on "conventional" low-T chemistry would help isolate effect of excited species reactions more reliably.