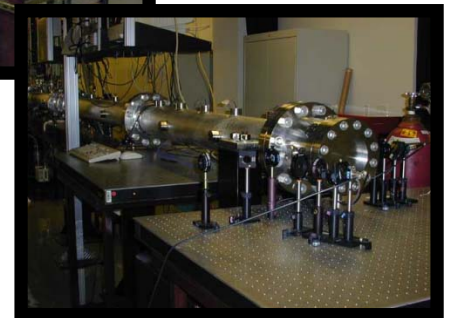
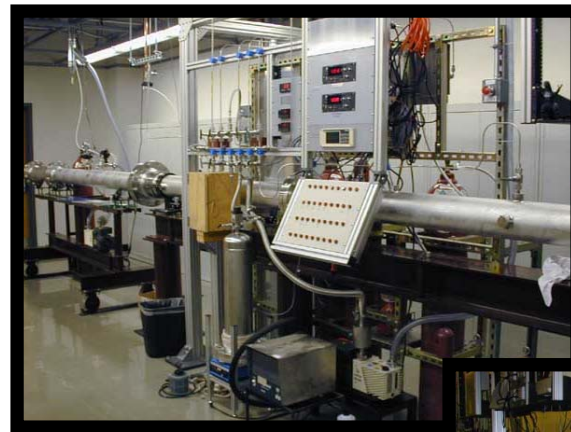
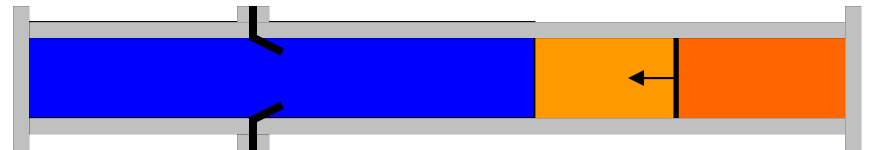


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

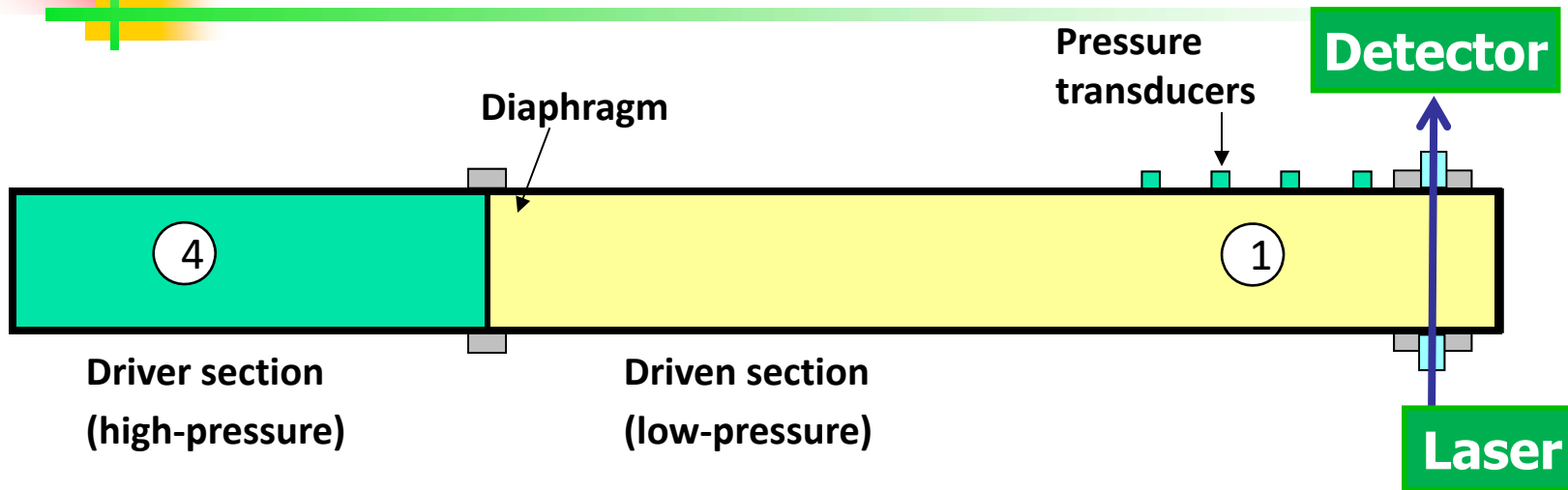
Lecture 11: Shock Tube Techniques/Applications

Motivation: Shock tubes with lasers is a chemical kinetics research frontier!

1. Introduction to Shock Tubes
2. Vibrational Relaxation
3. Ignition Studies
4. Advances in Shock Tube Modeling



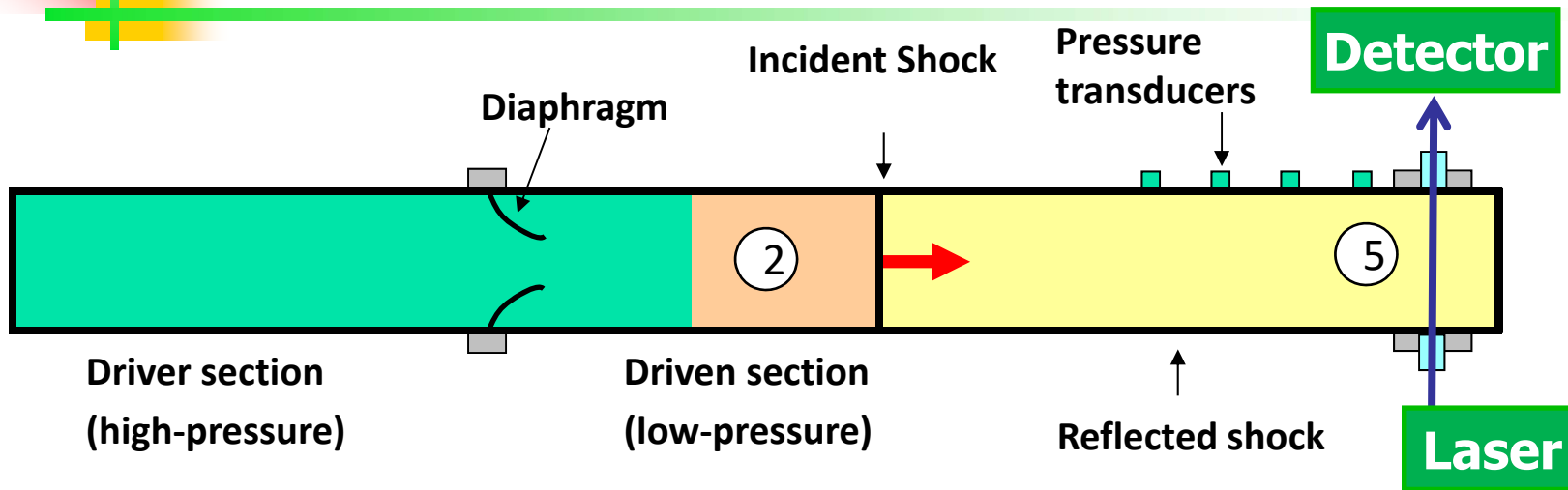
1. Introduction to Shock Tubes



Basic concept:

- High-pressure driver gas expands upon diaphragm opening, creating shock wave
- Test gas is instantaneously compressed and heated to combustion temperatures by incident and reflected shocks
- High-temperature experiments monitored near endwall

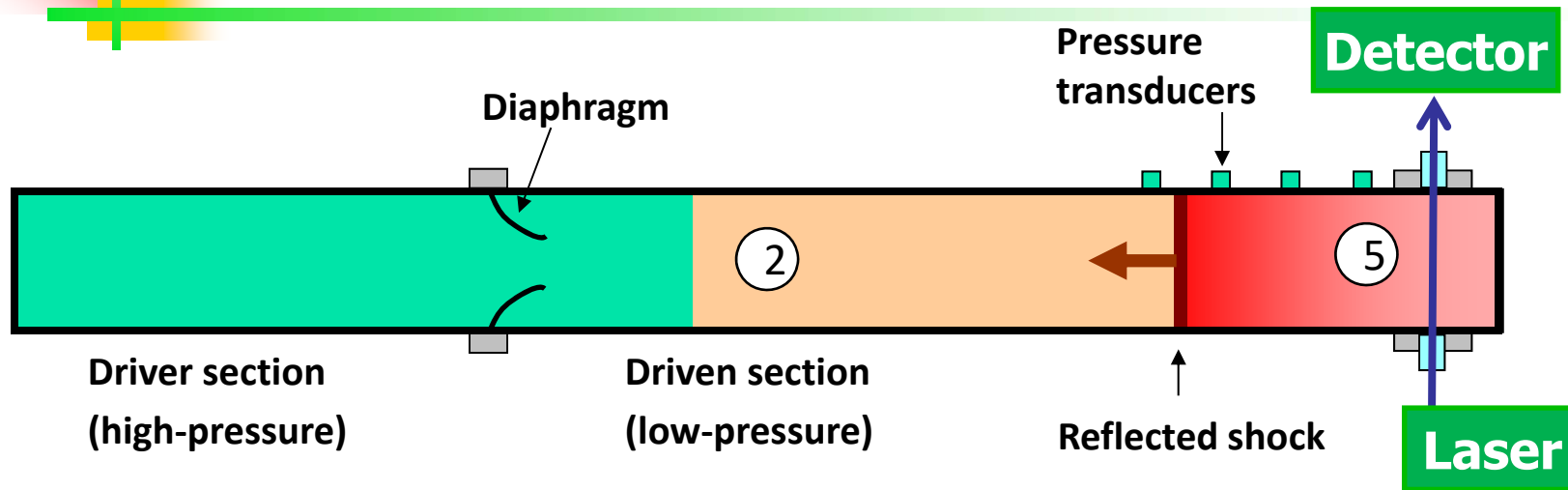
1. Introduction to Shock Tubes



Basic concept:

- High-pressure driver gas expands upon diaphragm opening creating shock wave
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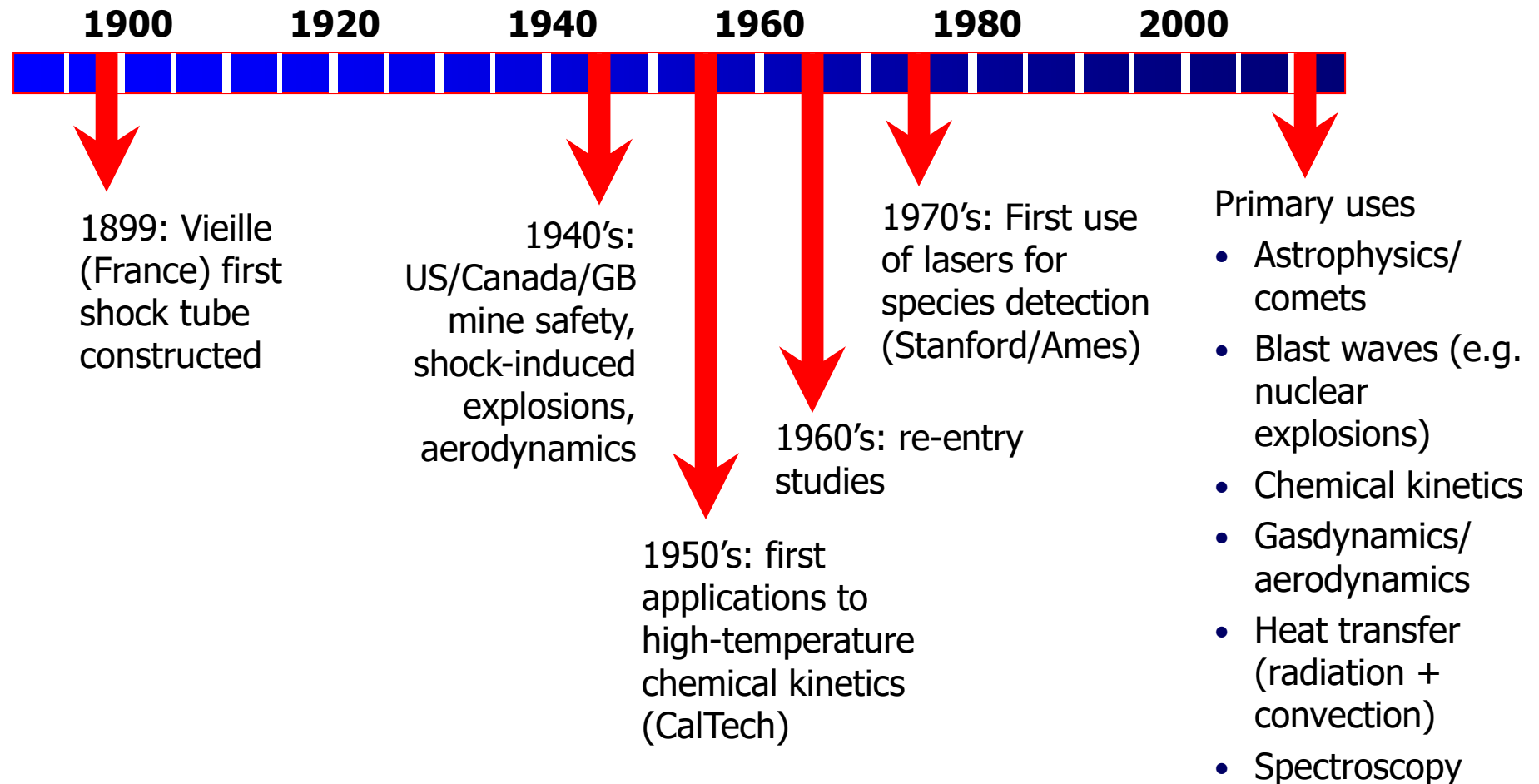
1. Introduction to Shock Tubes



Shock Tube Characteristics:

- Instantaneous heating/compression from shock waves
- Accurately known incident- and reflected-shock conditions (from incident shock M_s)
- Wide range of post-reflected shock T and P (600-4000 K, 0.1-1000 atm)

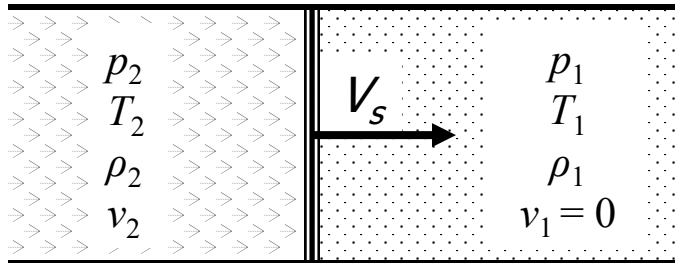
1. Introduction to Shock Tubes



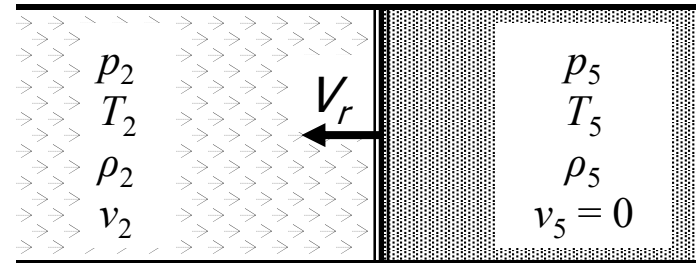
1. Introduction to Shock Tubes

1-D Shock Wave Theory

Laboratory-fixed coordinates



Incident shock



Reflected shock

- Incident shock speed governed by diaphragm burst pressure

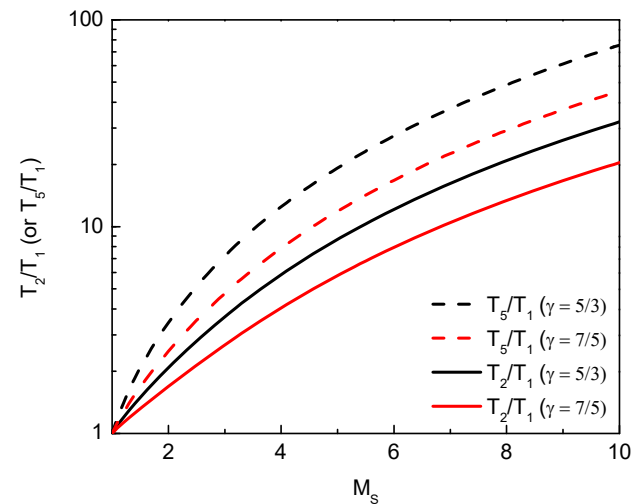
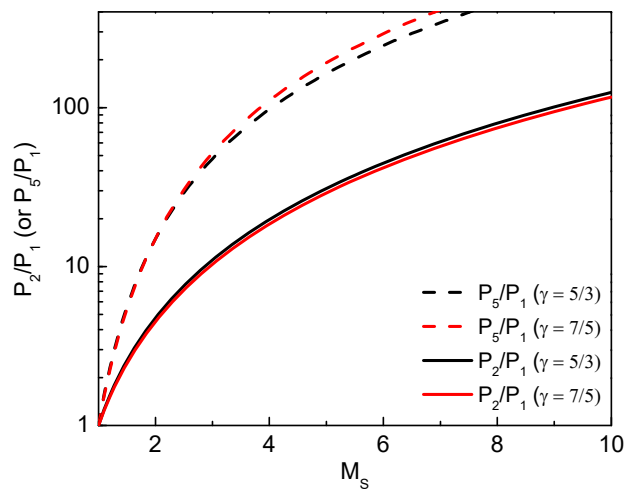
$$\frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left\{ 1 - \left(\frac{\gamma_4 - 1}{\gamma_1 + 1} \right) \left(\frac{a_1}{a_4} \right) \left(M_1 - \frac{1}{M_1} \right) \right\}^{-\left(\frac{2\gamma_4}{\gamma_4 - 1} \right)}$$

- Boundary condition $u_5 = 0$ determines the speed of the reflected shock
- All Region 5 conditions governed by incident shock speed
- See Gaydon and Hurle

1. Introduction to Shock Tubes

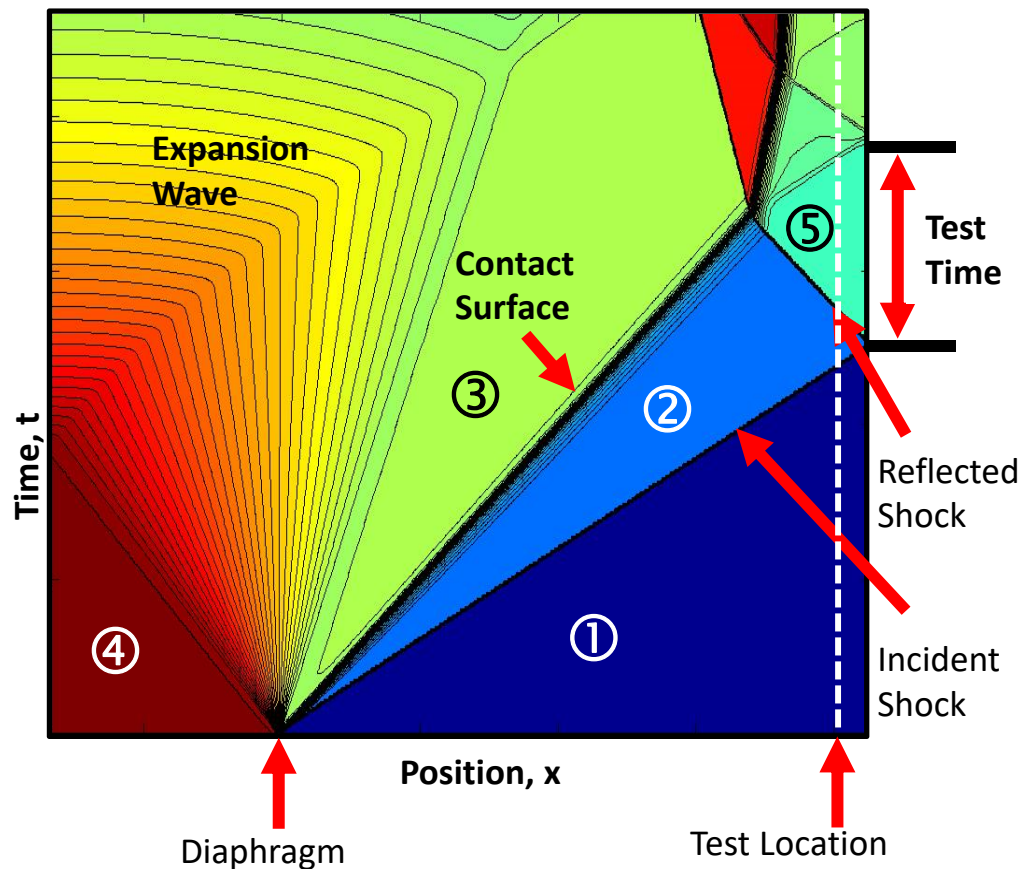
Shock Jump Values

γ	M_1	P_2/P_1	P_5/P_2	T_2/T_1	T_5/T_2	ρ_2/ρ_1	ρ_5/ρ_2	W_R/W_S
7/5	2.95	10	4.95	2.62	1.76	3.82	2.82	0.423
	6.56	50	7.12	9.31	2.28	5.37	3.11	0.351
	∞	∞	8.00	∞	2.29	6.00	3.50	0.333
5/3	2.87	10	4.22	3.42	1.94	2.92	2.17	0.589
	6.34	50	5.54	13.4	2.37	3.72	2.31	0.517
	∞	∞	6.00	∞	2.40	4.00	2.50	0.500

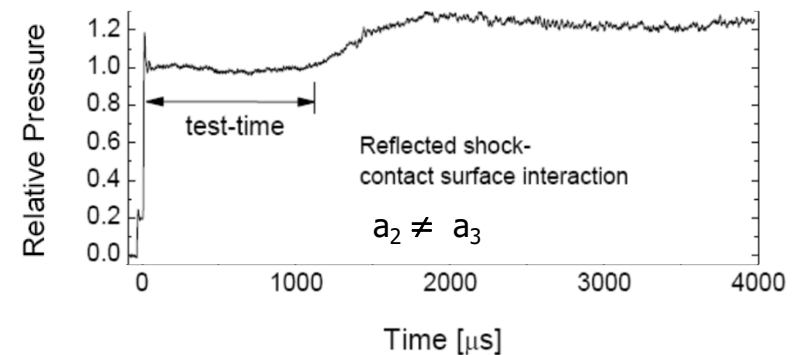


1. Introduction to Shock Tubes

Test Time in Reflected-Shock Experiments

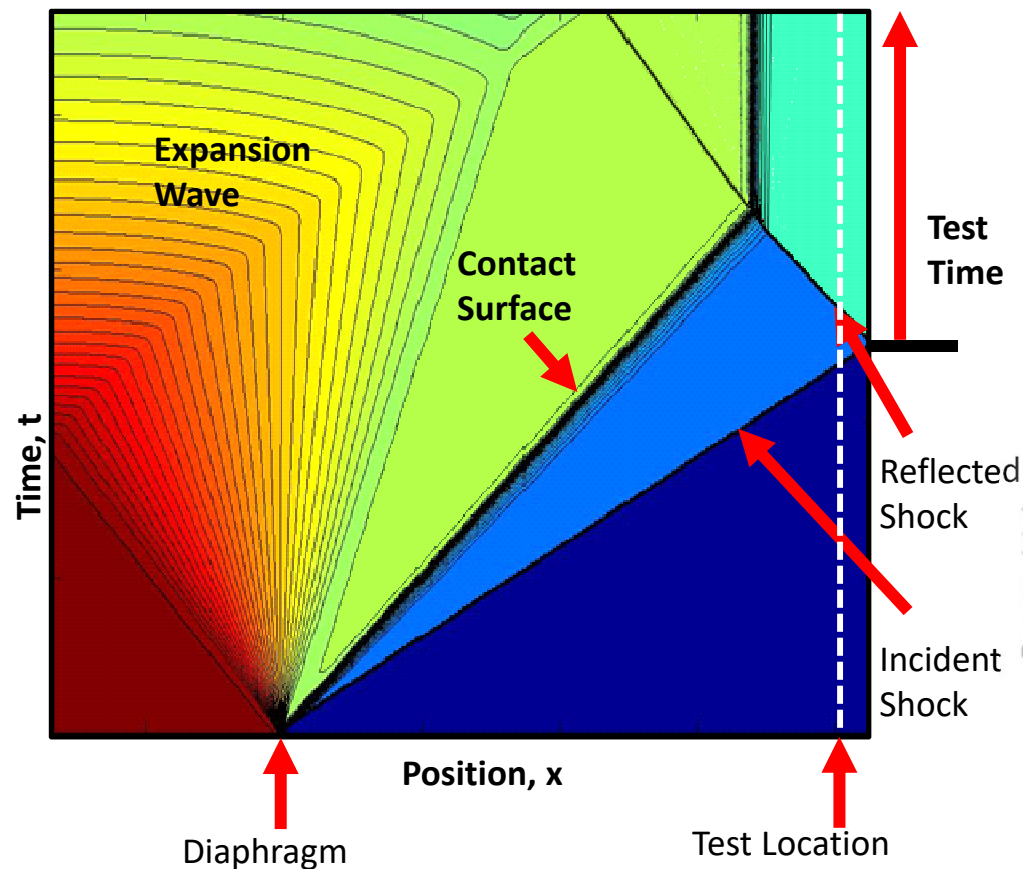


- Particles are stationary behind the reflected shock:
 - lab time = particle time
- Test time is limited by the reflected shock interaction with the contact surface
 - Typical test time $\sim 1-3$ ms

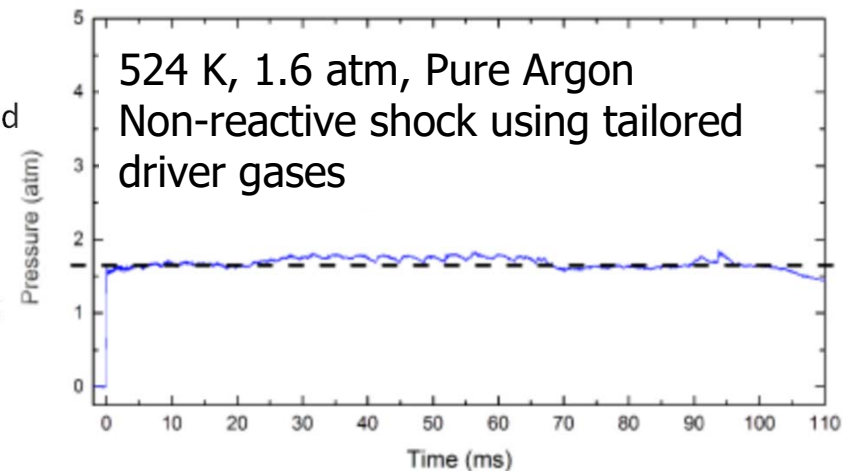


1. Introduction to Shock Tubes

Test Time in Reflected-Shock Experiments



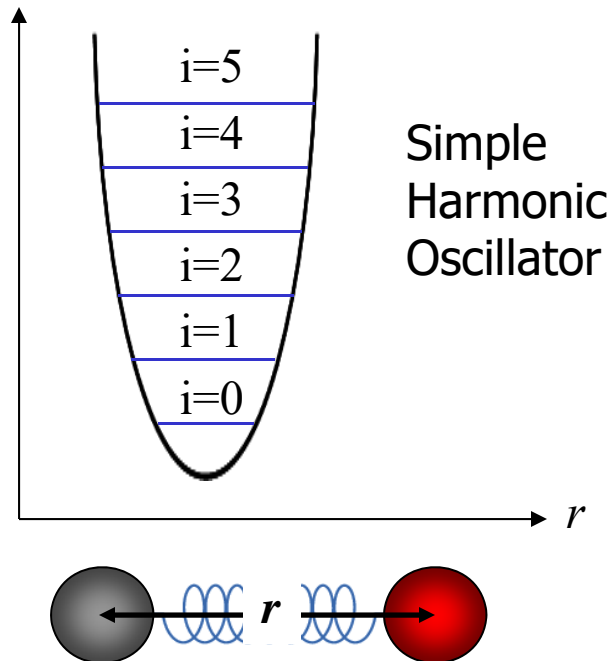
- Tailored driver gases optimize the reflected-shock-contact surface, increasing the test time
 - Tailored test times ≥ 10 ms



2. Vibrational Relaxation

Recall our previous lectures on the vibrational energy in diatomic molecules

- Use a simple harmonic oscillator model (HO)



- Molecular energy depends on inter-nuclei spacing and fundamental frequency

$$u = \frac{1}{2}kx^2, \quad x = r - r_e = \text{difference in nuclei spacing from equilibrium}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \quad k = \text{spring constant}; \quad \nu = \text{fundamental frequency of vibration}$$

- But energy levels are quantized!

$$\varepsilon_i = i h \nu = \text{energy in level } i$$

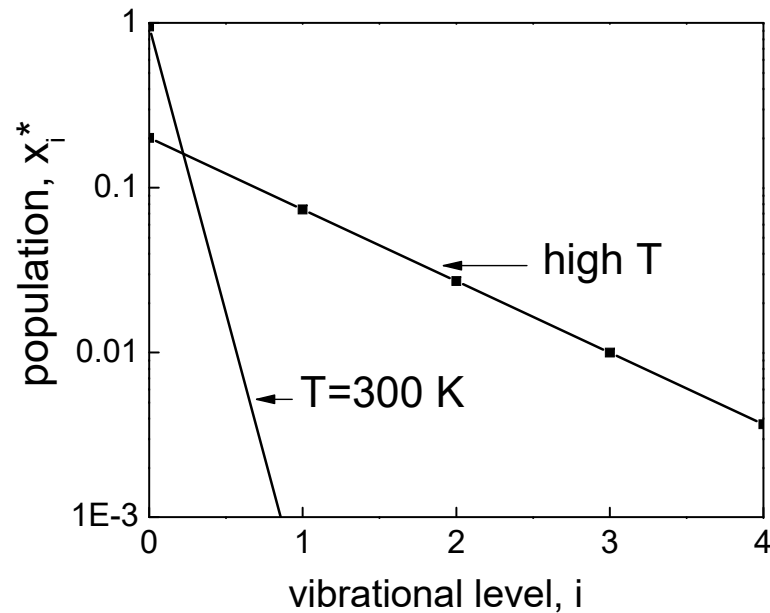
- Can use Boltzmann statistics (PGD) to determine distribution

$$x_i^* = \frac{N_i^*}{N} = \frac{e^{-i\theta_v/T}}{\left(Q = \frac{1}{1 - e^{-\theta_v/T}} \right)} = \text{fractional population in level } i$$

$$\text{with } \theta_v = \frac{h\nu}{k} = \frac{hc}{k} \left(\omega = \frac{1}{\lambda} \right) = \text{characteristic vibrational temperature}$$

$$e_v = \frac{R\theta_v}{e^{\theta_v/T} - 1} = \text{average vibrational energy per molecule}$$

2. Vibrational Relaxation



Vibrational energy distribution function (from Boltzmann statistics)

$$x_i^* = \frac{N_i^*}{N} = \frac{e^{-i\theta_v/T}}{\left(Q = \frac{1}{1 - e^{-\theta_v/T}}\right)} = \text{fractional population in level } i$$

- More molecules in lower vibrational levels than in high vibrational levels
- Higher energy levels get populated at higher temperatures
- Temperature refers to the vibrational temperature ($T = T_v$), the same as translational temperature in vibrational equilibrium
- If $T_v \neq T_{\text{trans}}$ then vibrational energy transfer will occur until the system reaches equilibrium
→ **vibrational relaxation!**



2. Vibrational Relaxation

V-T Energy Transfer

- How fast does relaxation occur?
- Rate of relaxation follows the Bethe-Teller relationship

$$dE_v/dt = \frac{E_v^*(T_{tr}) - E_v}{\tau}$$

E_v = vibrational energy (e.g. per mole, unit mass, etc.)

$E_v^*(T_{tr})$ = vibrational energy at translational temperature (i.e. equilibrium)

- Vibrational energy (E_v) changes at a rate proportional to deviation from the equilibrium value (E_v^*)

- Dependencies

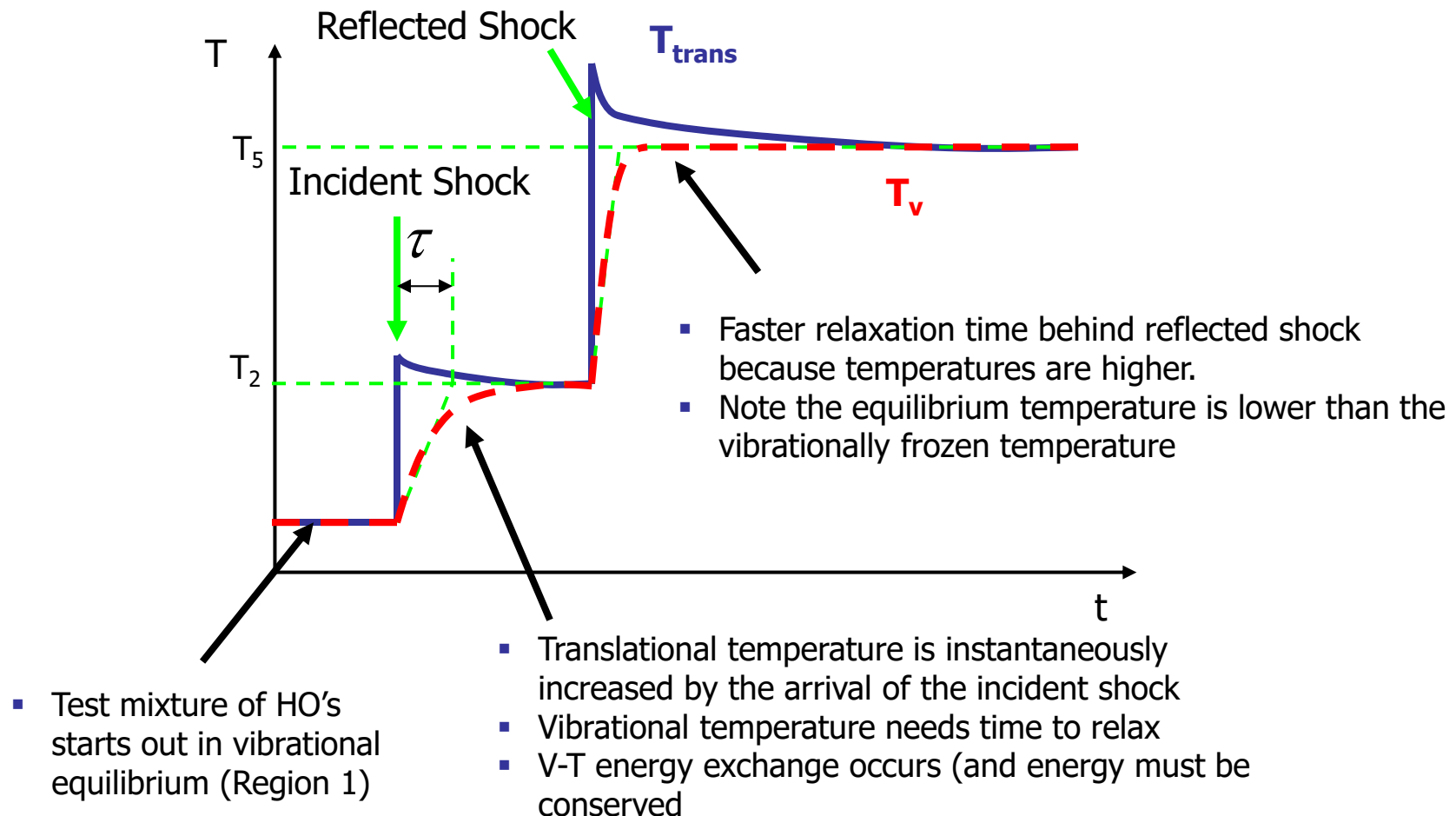
- Relaxation time constant:
$$\tau = \frac{1}{ZMP_{1,0} \left(1 - e^{-\theta_v/T}\right)}$$

- As T increases, the relaxation time constant decreases
- The relaxation time constant is independent from the deviation from equilibrium
- The relaxation time constant is also independent of the initial vibrational distribution

- How can we measure τ ?

2. Vibrational Relaxation

Vibrational Relaxation in Shock Tubes



2. Vibrational Relaxation

Shock Tube Studies of Vibrational Relaxation

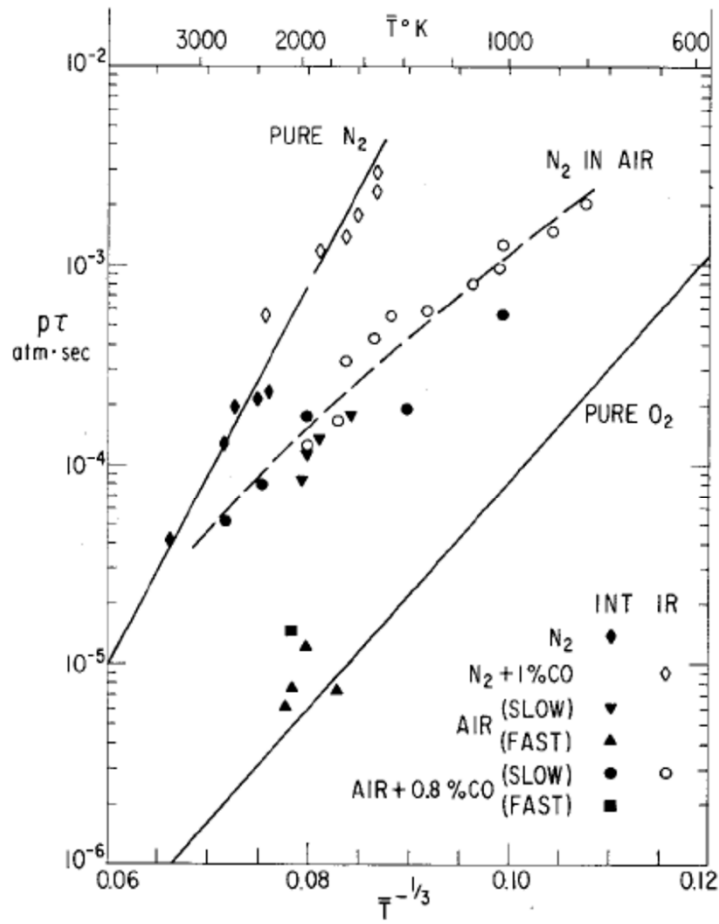


Fig. 1 Experimental data on vibrational relaxation of the components of air.

- Millikan and White were able to measure the vibrational relaxation speed of CO, O₂, N₂, and air at various temperatures using shock tubes
 - Seed small amounts of CO into the test gas
 - IR emission of CO near 4.7 microns
 - Optical interferometry to monitor pressure/density change due to N₂/O₂ relaxation

White and Millikan, *AIAA Journal* 1964.

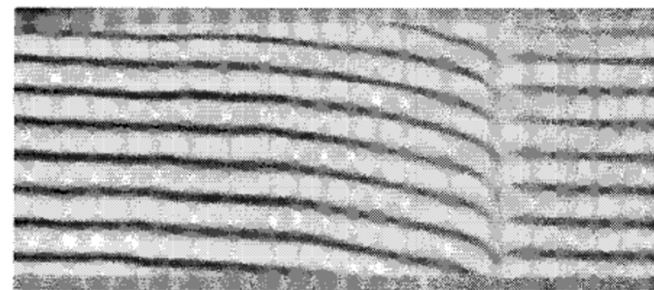


Fig. 2 Interferogram of a Mach 5.13 shock wave traveling to the right into 0.1 atm of air. A density increase displaces the interference fringes upward. The vertical field of view is 2.7 cm and includes the upper surface of the shock tube. The sharper fringe curvature immediately behind the shock front is attributed to vibrational relaxation of O₂.



2. Vibrational Relaxation

- **Modern Experiments with Laser Diagnostics**

Goal:

- High-temperature O₂ vibration relaxation rates

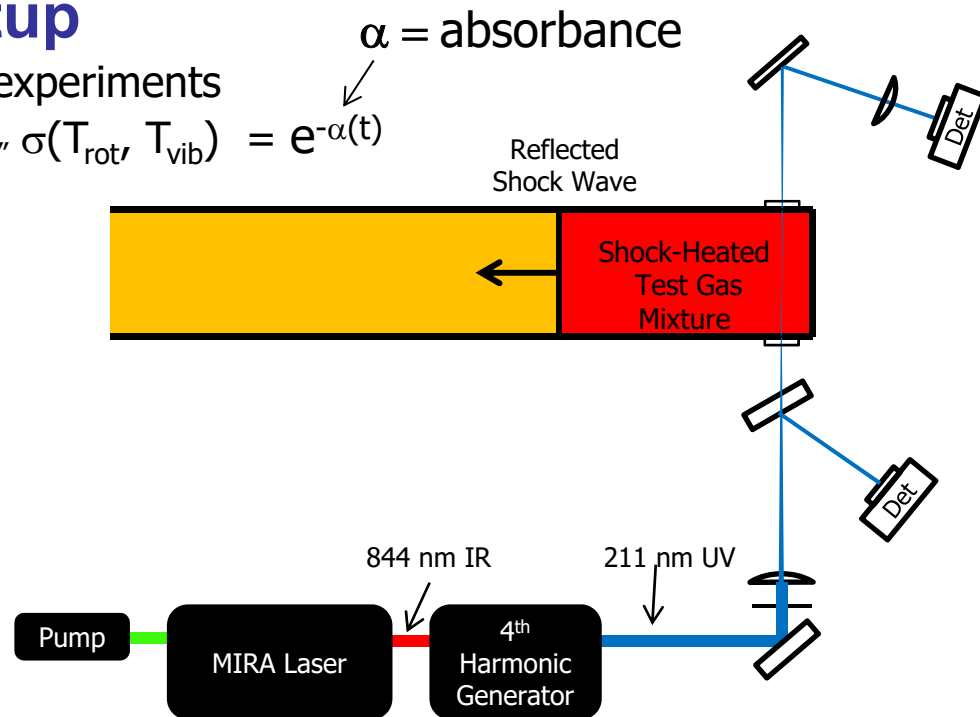
Experimental Strategy:

- Shock heat highly diluted mixtures of O₂ in Ar
- New diagnostic (MIRA laser) to measure O₂ in deep UV (Schumann-Runge) at 206 to 245 nm, probing different vibrational levels

2. Vibrational Relaxation

Experimental Setup

- Reflected shock absorption experiments
- Beer's law: $(I/I_0)_\lambda = \exp(-n_{v''} \sigma(T_{\text{rot}}, T_{\text{vib}})) = e^{-\alpha(t)}$
- Measure $\alpha(t)$
- Infer $n_{v''}(t)$ and $e_v(t)$



MIRA operating range: 206-1000 nm

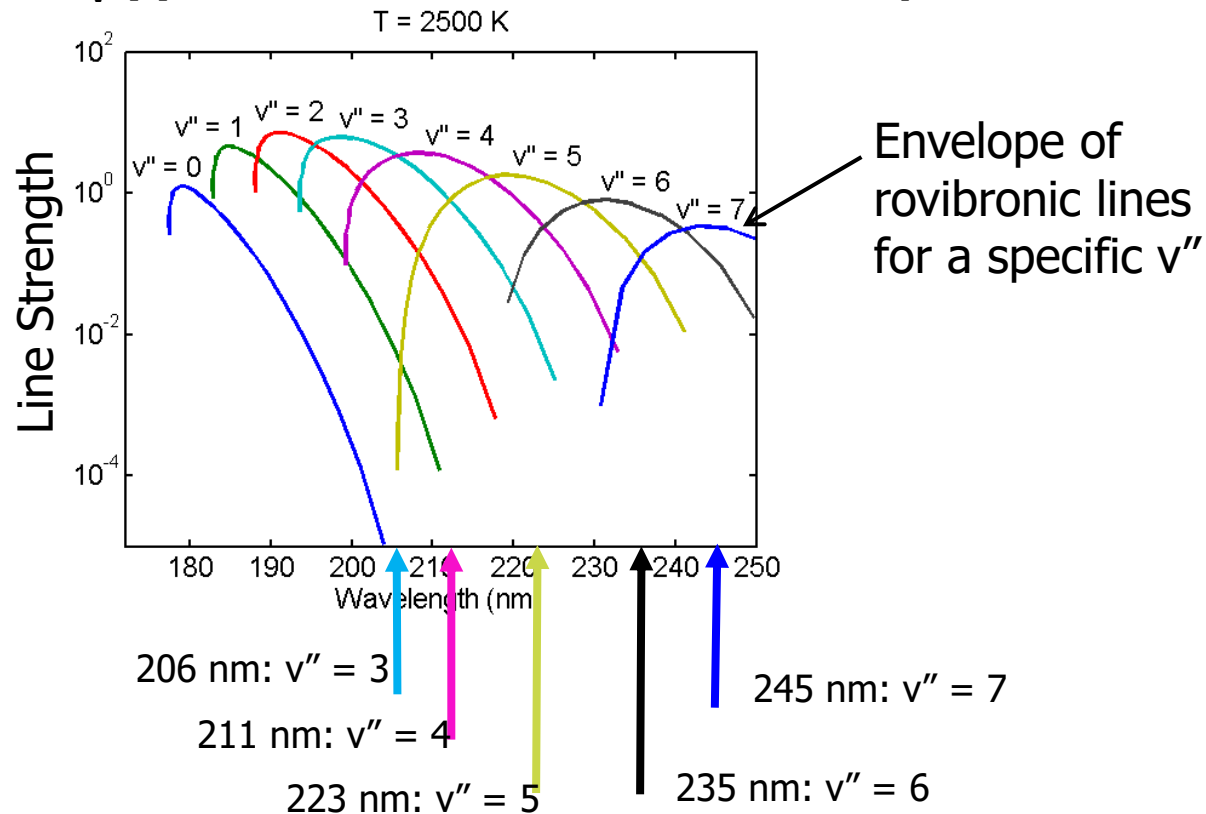
Pulse rate: 80 MHz, equivalent to CW

Average power: 2-20 mW at 206 nm to 245 nm

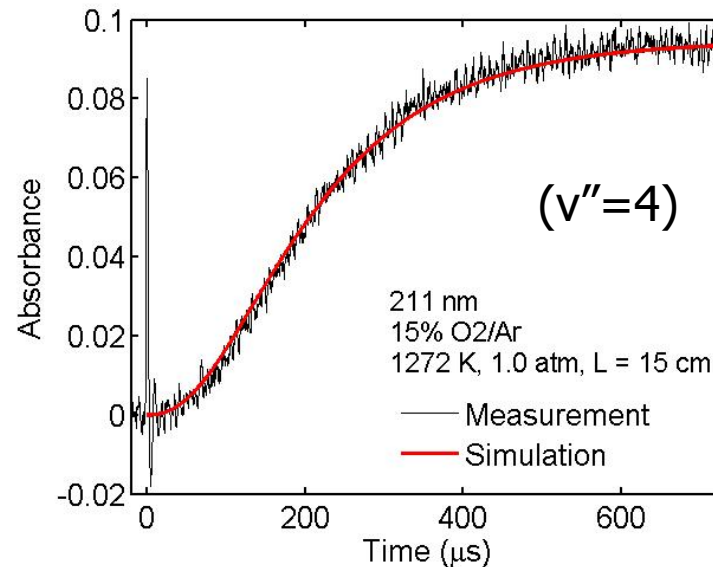
How does this relate to O₂ vibrational populations?

2. Vibrational Relaxation

- **Schumann-Runge O₂ system** ($B^3\Sigma_u^- \leftarrow X^3\Sigma_g^+$) has overlapping features
- Select wavelengths sensitive to specific v''
- Laser experiments measure total absorption at fixed λ , involves many lines
- **Goal: Infer $n_{v''}(t)$ for $v' = 3-7$ from absorbances at peak λ 's**

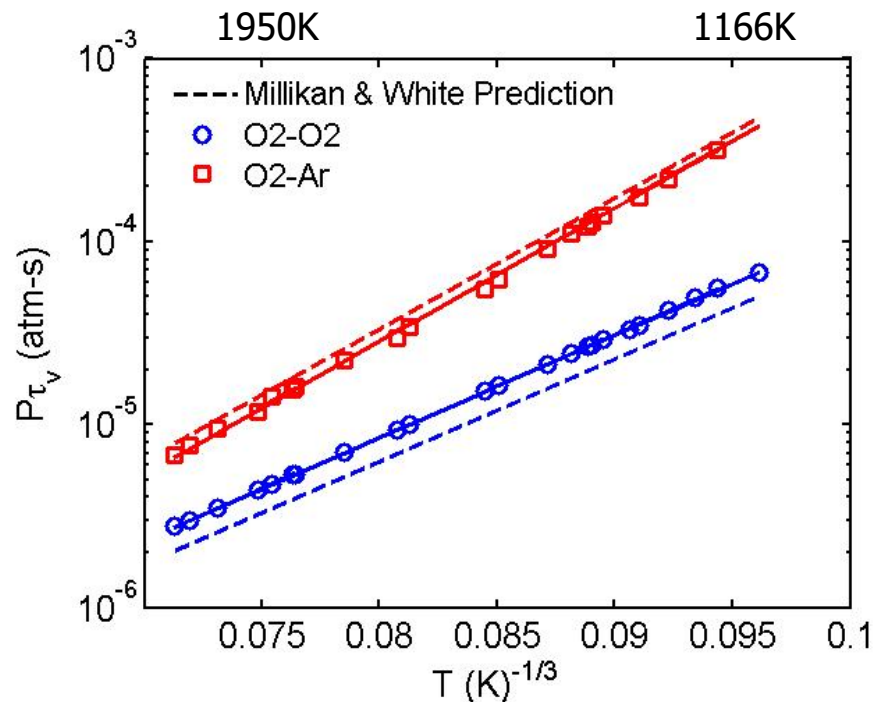


2. Example O₂ Data and Model



- excellent signal-to-noise ratio (noise $\sim 0.3\%$ absorbance)
- High-accuracy determination of X_{O_2} , T_5 , P_5
- high-accuracy measurement of τ_{vib} !
- Initial data support an evolving Boltzmann distribution for e_{vib}
- t_{vib} can be plotted on a Landau-Teller plot

2. Landau-Teller Plot



Mixture Rule for τ : $(1/P\tau)_{\text{mix}} = \sum X_j/P\tau_j$

O₂ vibrational relaxation measurements

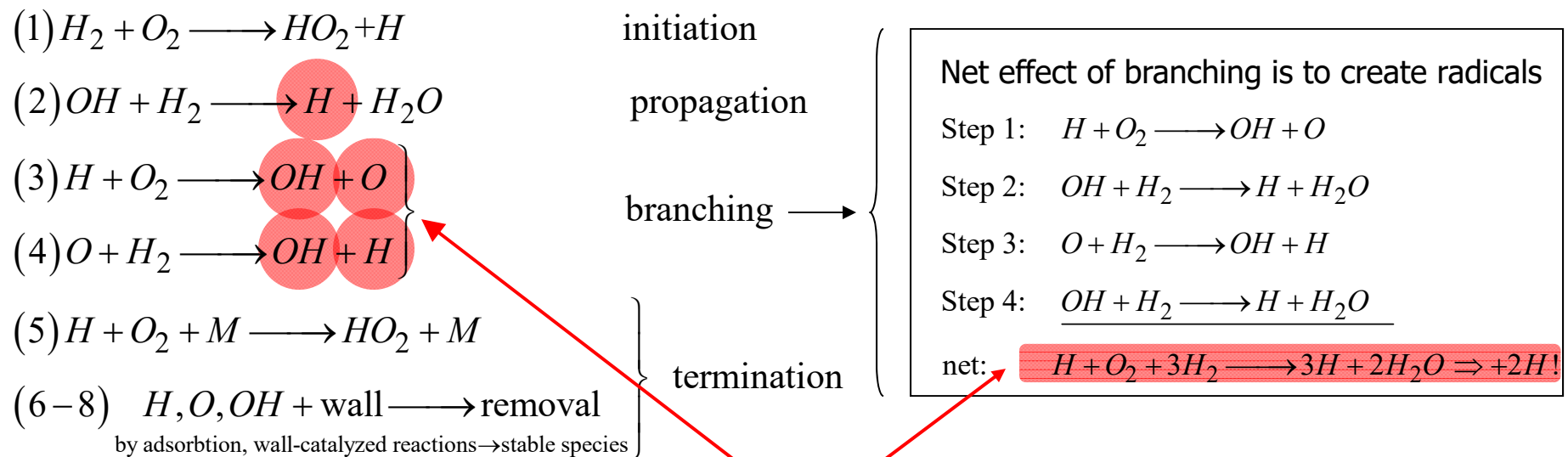
- Current work in close agreement with classic studies (**Millikan and White (1963)**), but with much lower scatter
- Experiments with varying O₂ fraction → $\tau_{VT}(\text{O}_2\text{-O}_2)$ and $\tau_{VT}(\text{O}_2\text{-Ar})$



3. Ignition Studies

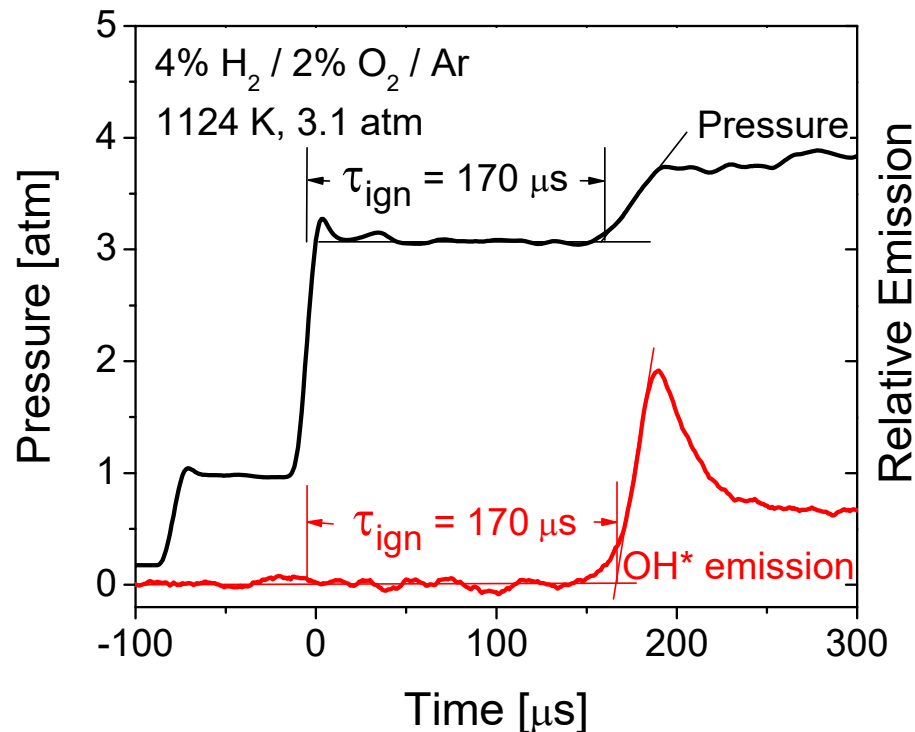
1. Kinetics of branched chain reactions
2. Definition of ignition
3. Examples

3.1. Kinetics of Branched Chain Reactions: Basic Mechanism for Hydrogen Oxidation



- Build up of a radical pool during oxidation
- This characterizes ignition!
- Also exothermic reactions generate heat release/pressure increase

3.2. Definition of Ignition Time

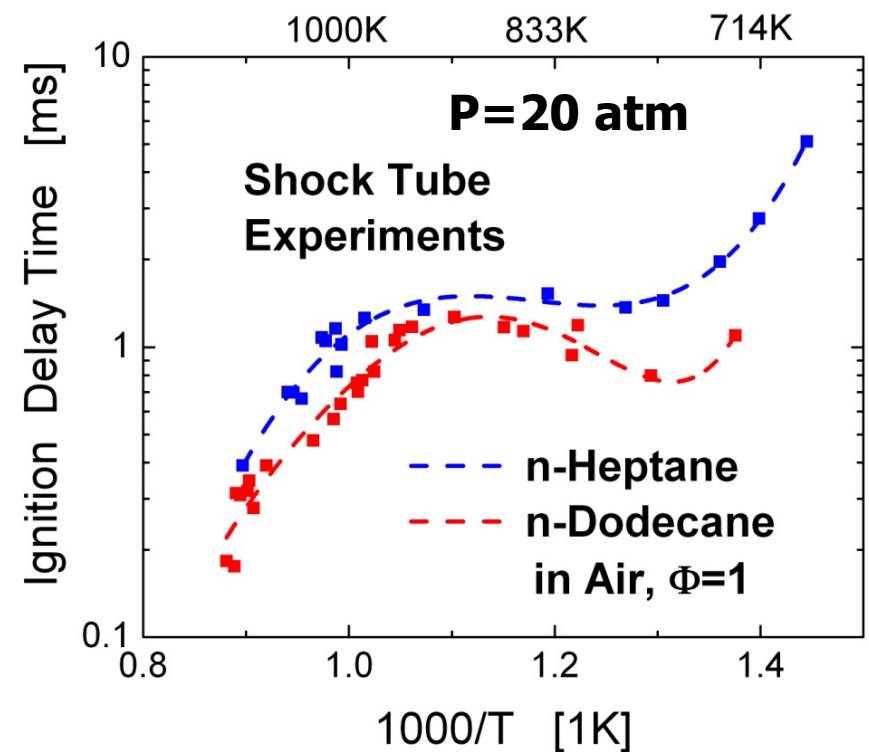
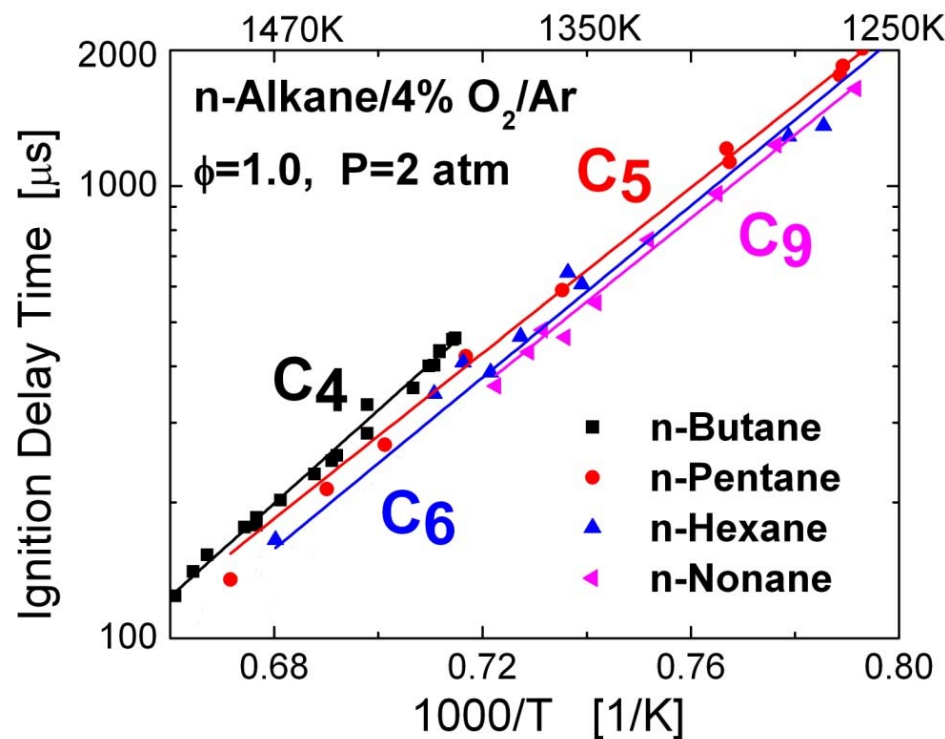


- **Ignition delay time in reflected shock experiments:** time between passing of the reflected shock and onset of ignition
- **Onset of ignition:** linearly extrapolating the point of steepest rise back in time to the pre-ignition baseline

- Measure through $P_5(t)$ and $\text{OH}^*(t)$ emission at 306 nm (A-X)
- Close agreement of pressure and emission measurement

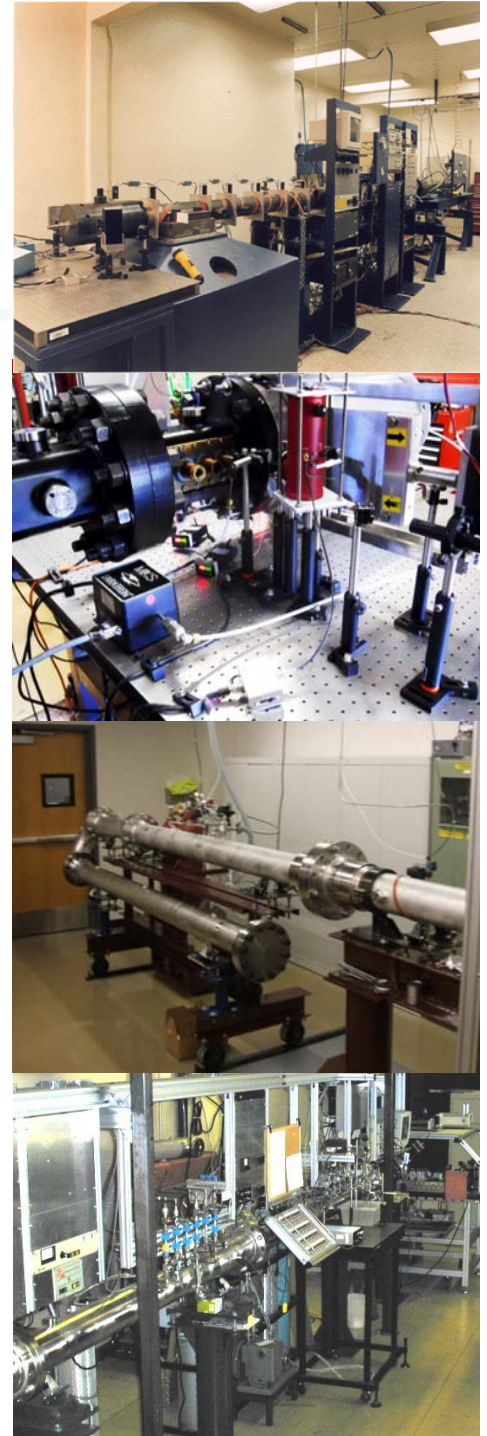
3.3. Examples

- Able to examine correlations for ignition times in different alkanes
- Negative temperature dependence of ignition times is seen at low-intermediate temperatures



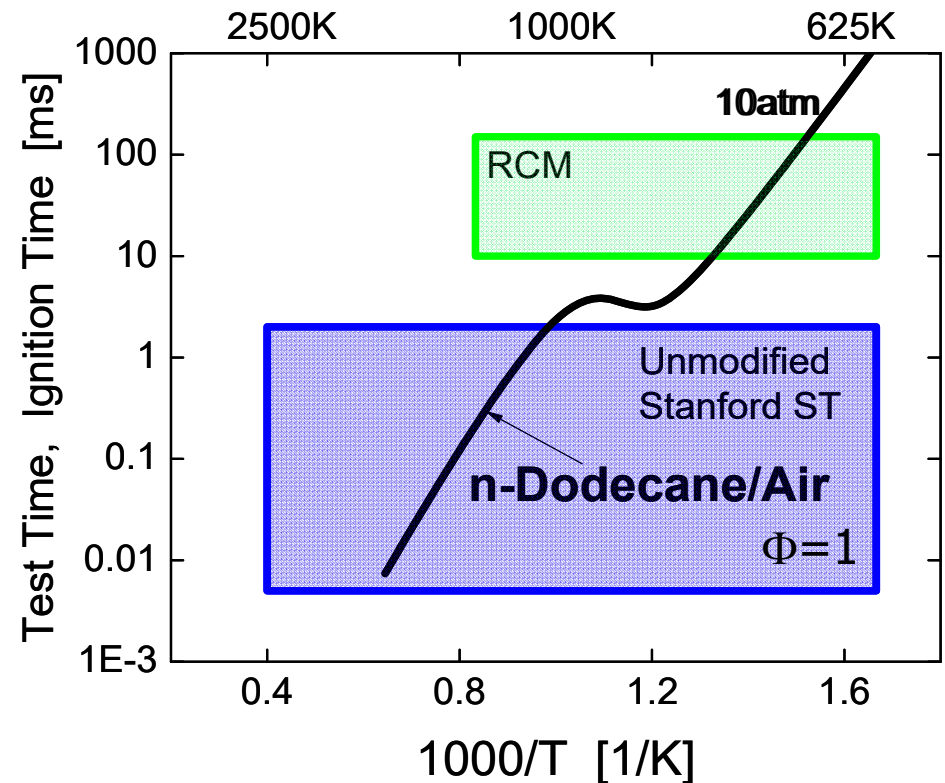
4. Advances in Shock Tube Methods

- 1. Extended drivers & tailored gas mixtures for longer test times**
- 2. Driver inserts for improved spatial and temporal uniformity**
- 3. New approaches to reactive gas modeling**



4.1. Extended drivers & tailored gas mixtures for longer test times

- Conventional shock tube operation: $\sim 1\text{-}3\text{ ms}$ test time
- No overlap with RCM operation $\sim 10\text{-}150\text{ ms}$ test time

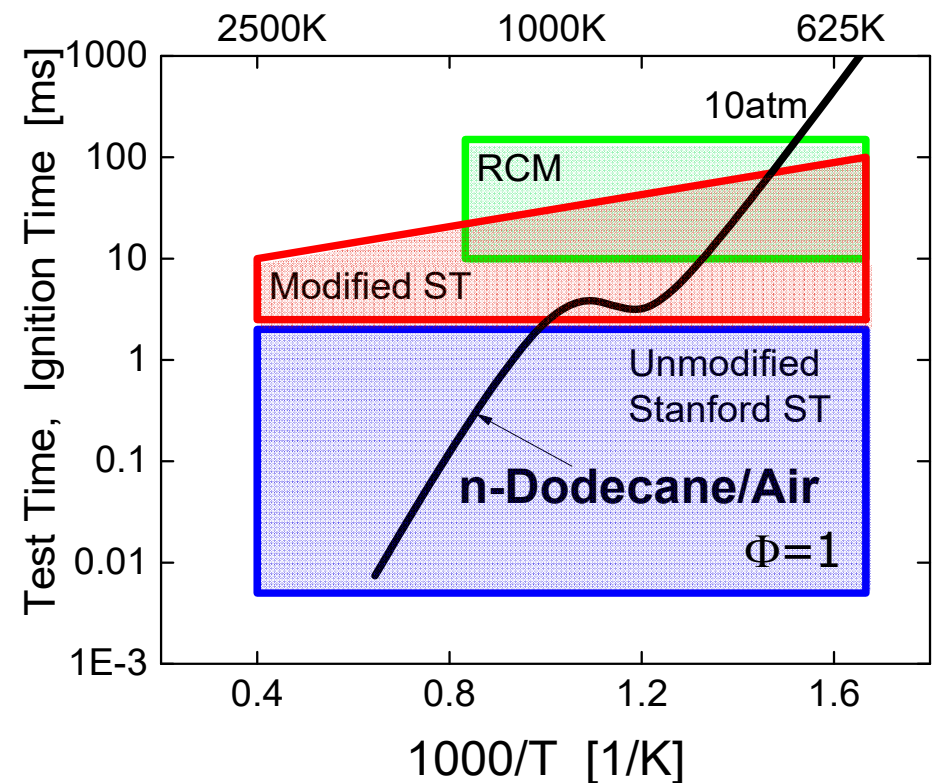


4.1. Extended drivers & tailored gas mixtures for longer test times

- Longer driver length and tailored gas mixtures can provide longer test times (50+ ms)



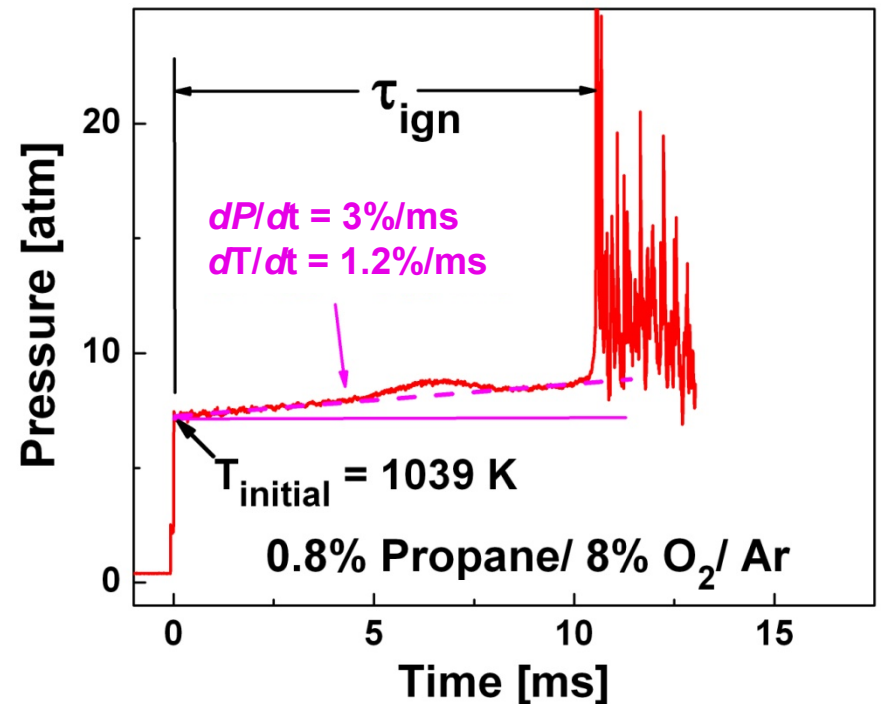
2x Driver Extension



- Shock tubes now can overlap with RCMs

4.2. Driver inserts for improved spatial and temporal uniformity

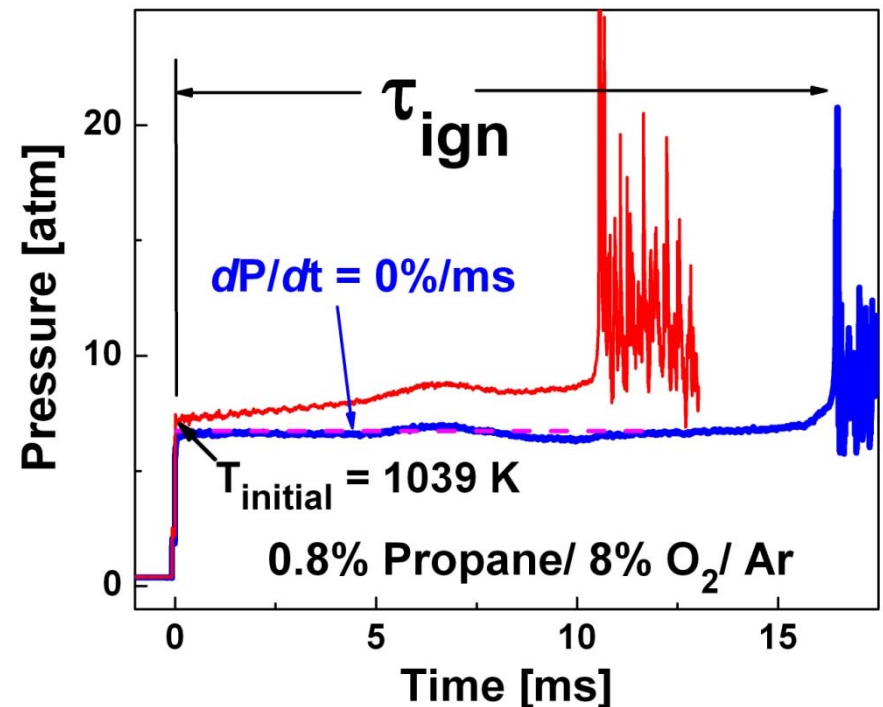
- Problem:** boundary layers and attenuation induce dP/dt and dT/dt that change ignition times



- Solution:** Driver inserts that modify flow to achieve uniform T and P at long test times

4.2. Driver inserts for improved spatial and temporal uniformity

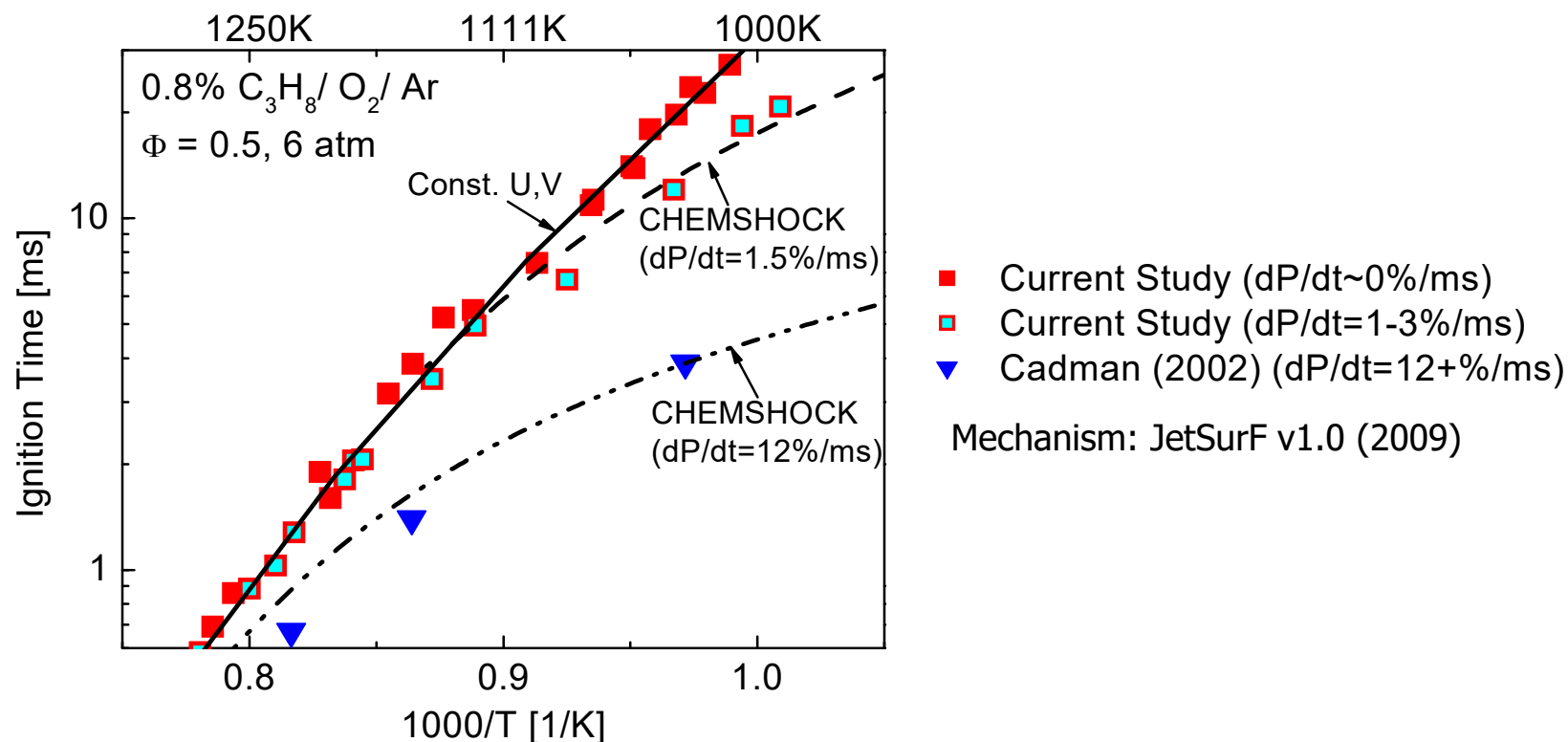
- **Result:** $dP/dt = 0$ prior to ignition
- Improved τ_{ign} for comparison with simulations



- **Solution:** Driver inserts that modify flow to achieve uniform T and P at long test times
- Example: Propane Ignition

4.2. Driver inserts for improved spatial and temporal uniformity

- Modifications yield improved ignition delay times for propane



- $dP/dt = 0$ data provide improved targets for constant U,V simulations
- Experimentalists must report facility dP/dt to allow modelers to make useful comparisons with detailed mechanisms, e.g. via CHEMSHOCK



4.3. New approaches to reactive gas modeling

Reactive Gasdynamics Modeling: The Problem

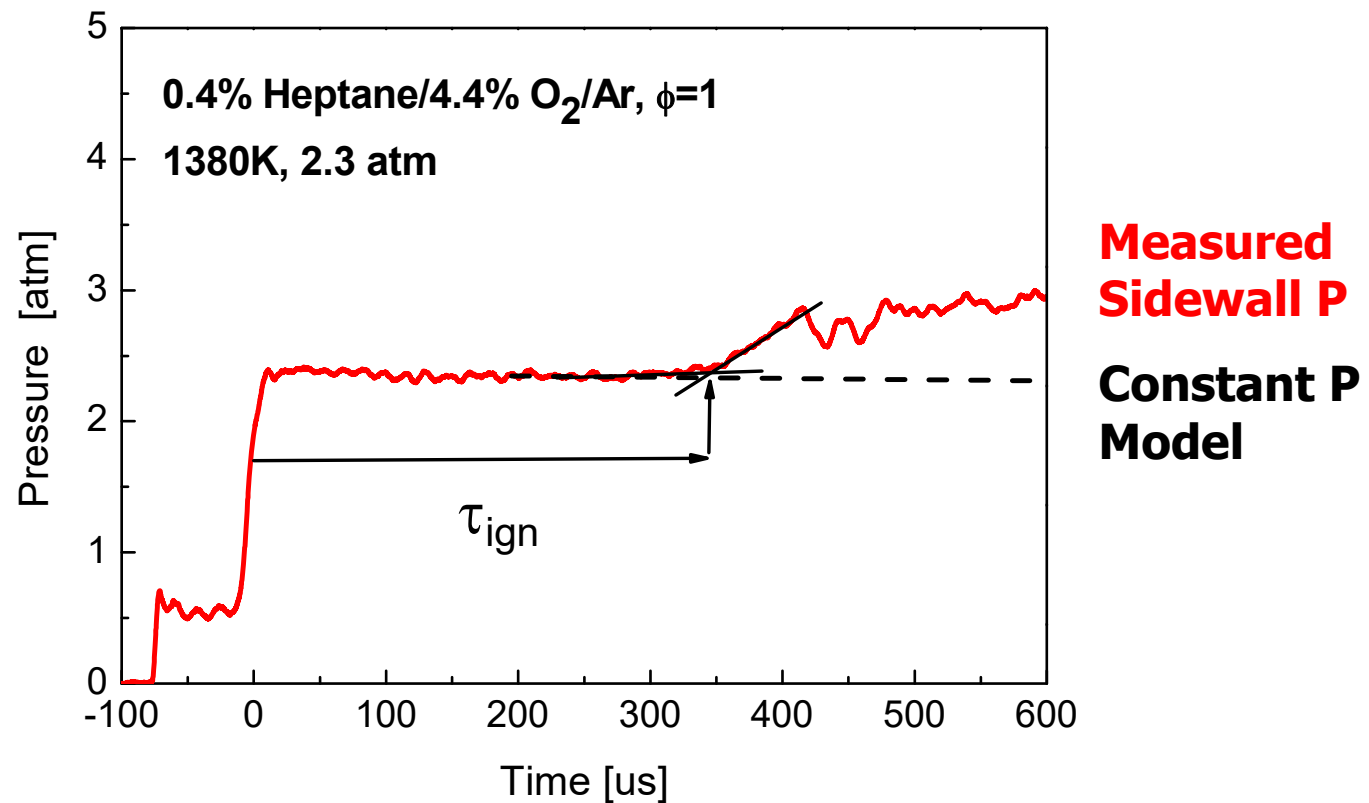
- Most current reflected shock modeling assumes Constant Volume or Constant Pressure

But:

- Reflected shock reactions are NOT Constant V or Constant P processes!
- Example: Heptane Ignition

4.3. New approaches to reactive gas modeling

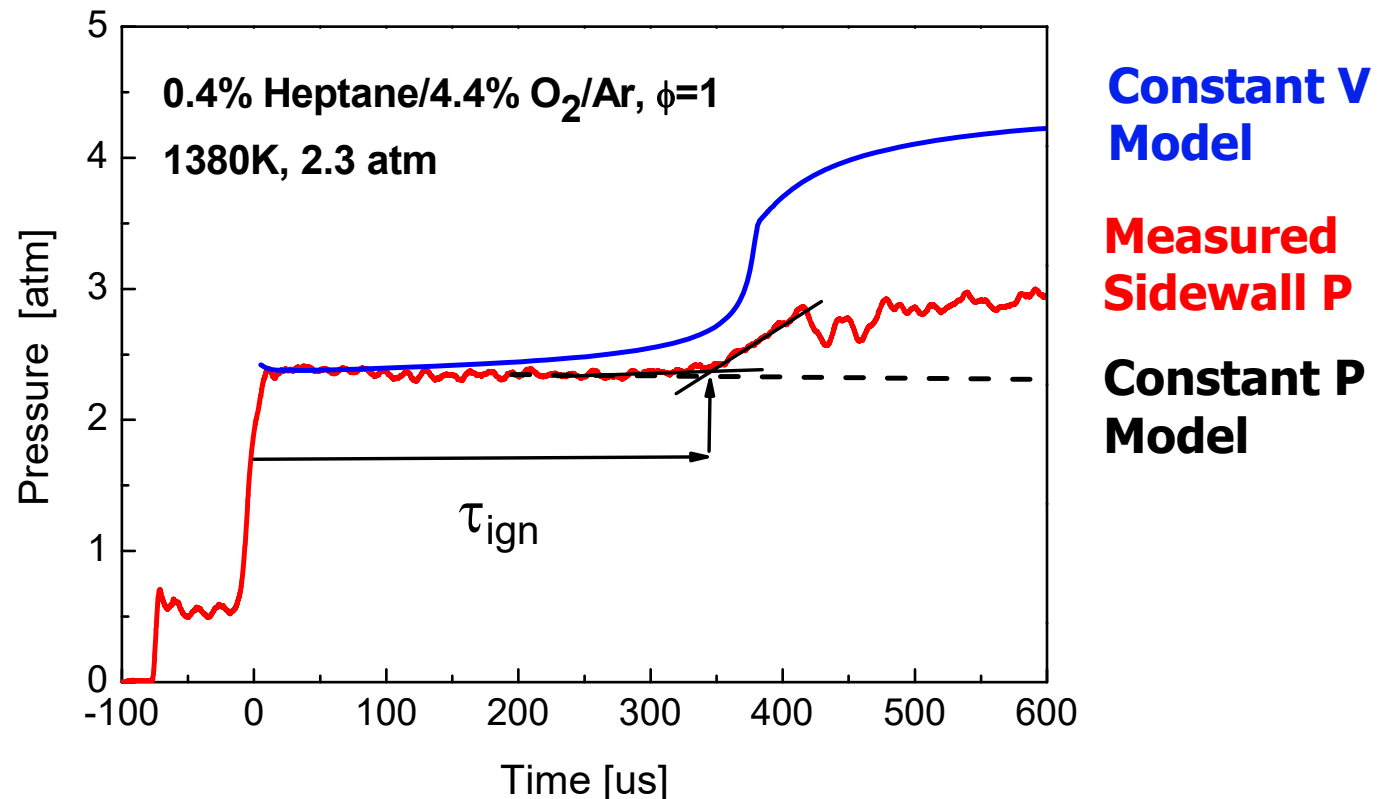
- Effect of Energy Release on P Profiles: n-Heptane Oxidation



- This is not a Constant P process!**

4.3. New approaches to reactive gas modeling

- Effect of Energy Release on P Profiles: n-Heptane Oxidation



- This is not a Constant P process!
- Also not a Constant V process!
- So how can entire process be modeled?

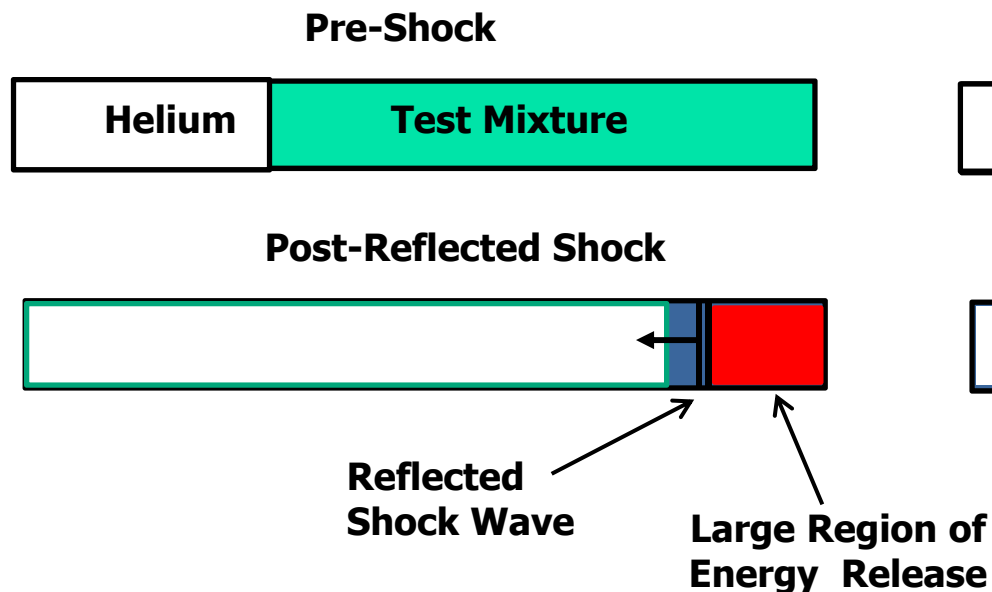
4.3. New approaches to reactive gas modeling

- **Proposed Solutions to Enable Modeling through Entire Combustion Event**
 - **Minimize fuel loading to reduce exothermically- or endothermically-driven T and P changes**
 - **enabled by high-sensitivity laser diagnostics**
 - **Use new constrained reaction volume (CRV) concept to minimize pressure perturbations**
 - **enables constant P (or specified P) modeling**

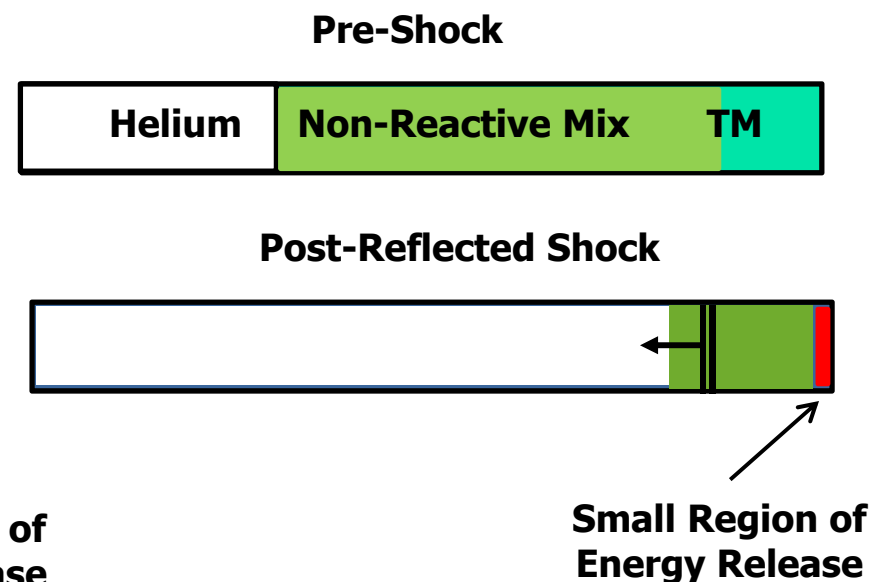
4.3. New approaches to reactive gas modeling

- Constrained Reaction Volume (CRV) Approach

Conventional Shock Tube



Constrained Reaction Volume

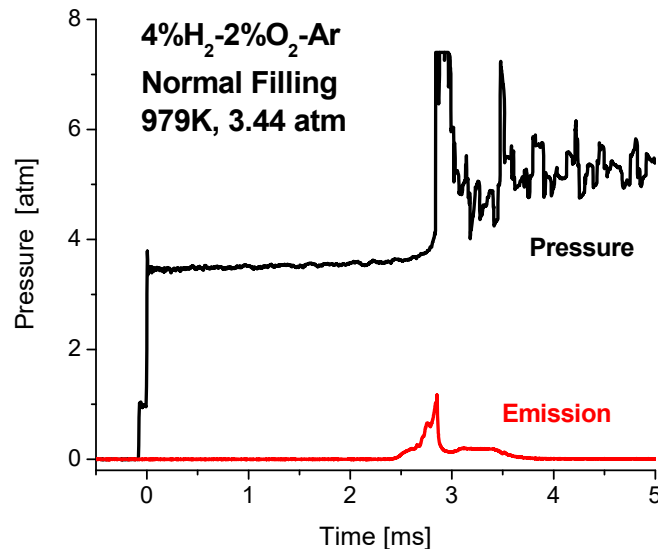


- Large reaction volume gives large energy release $\rightarrow \Delta P$ & ΔT
- CRV gives reduced energy release \rightarrow near-constant P
- Also eliminates any question of remote ignition!

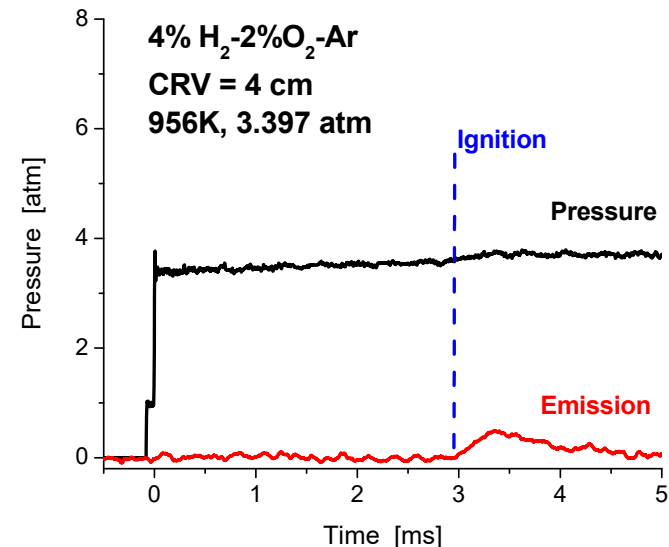
4.3. New approaches to reactive gas modeling

- Use of Constrained Reaction Volume (CRV) Approach
1st Example: Hydrogen Ignition at 950 K

Conventional Shock Tube



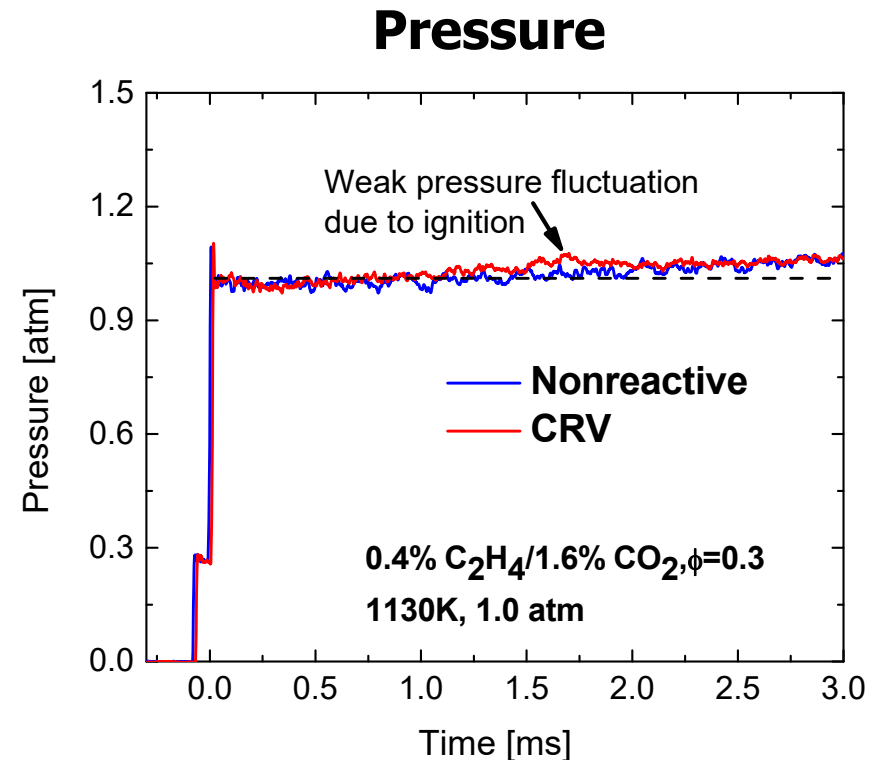
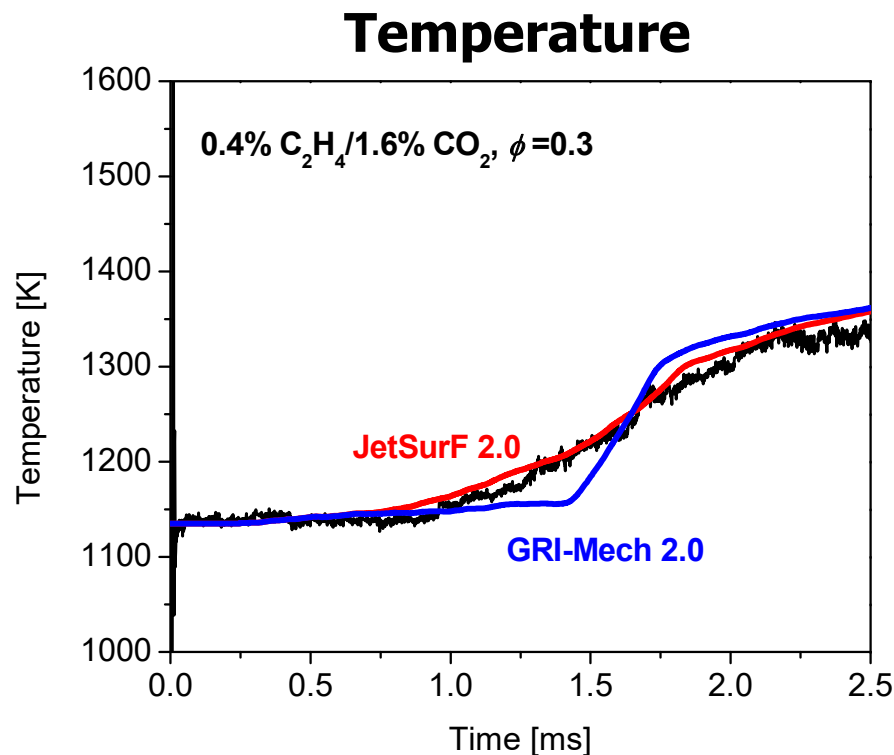
Constrained Reaction Volume



- Conventional ST exhibits large pressure change!
- CRV pressure nearly constant throughout experiment!
- Allows 1st kinetics modeling through ignition and combustion in non-dilute systems!

4.3. New approaches to reactive gas modeling

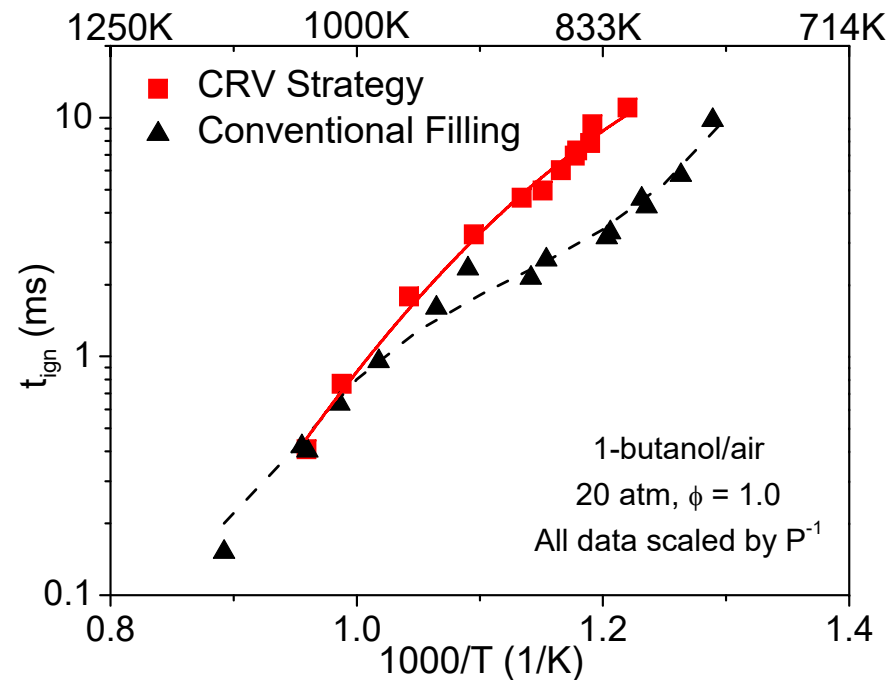
- Confirmation of CRV Approach
2nd Example: C₂H₄ Ignition, Temperature and OH



- Measured T validates CRV approach and illustrates power of T as a kinetics diagnostic

4.3. New approaches to reactive gas modeling

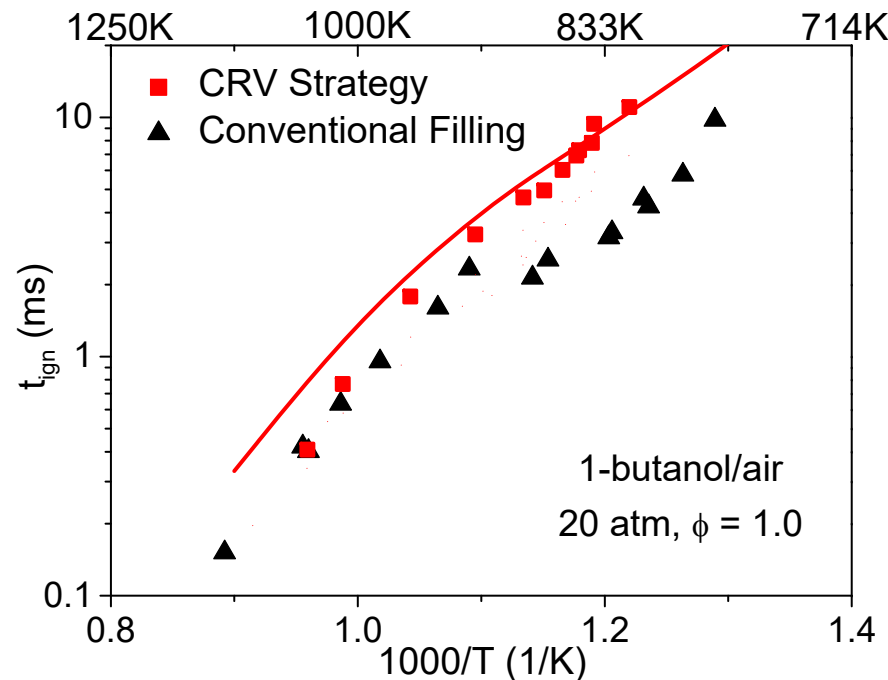
- 3rd Example: Low Temperature 1-Butanol Ignition Data Comparison of Conventional Filling and CRV Experiments



- CRV & conventional filling data agree at high T
- CRV yields longer delay times at lower T than conventional filling
- CRV provides true constant H, P data, conventional data are difficult to model

4.3. New approaches to reactive gas modeling

- 3rd Example: Low Temperature 1-Butanol Ignition Data Comparison of Conventional Filling and CRV Experiments



Solid Line:
Sarathy et al. (2012)

Current models are in
agreement with CRV
constant P data!

- CRV & conventional filling data agree at high T
- CRV yields longer delay times at lower T than conventional filling
- CRV provides true constant H, P data; conventional data are difficult to model



Next: Shock Tube Applications with Lasers

- Elementary Reactions
- Multi-Species Time-Histories