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

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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

Primary uses
- Astrophysics/comets
- Blast waves (e.g. nuclear explosions)
- Chemical kinetics
- Gasdynamics/aerodynamics
- Heat transfer (radiation + convection)
- Spectroscopy

1899: Vieille (France) first shock tube constructed

1940’s: US/Canada/GB mine safety, shock-induced explosions, aerodynamics

1950’s: first applications to high-temperature chemical kinetics (CalTech)

1960’s: re-entry studies

1970’s: First use of lasers for species detection (Stanford/Ames)

1940’s: First use of lasers for species detection (Stanford/Ames)
1. Introduction to Shock Tubes

1-D Shock Wave Theory

**Laboratory-fixed coordinates**

- Incident shock speed governed by diaphragm burst pressure

\[
\frac{p_4}{p_1} = \frac{2\gamma_1 M_1^2}{\gamma_1 + 1} \left( 1 - \left( \frac{\gamma_4 - 1}{\gamma_1 + 1} \right) \left( \frac{\alpha_1}{\alpha_4} \right) \left( M_1 - \frac{1}{M_1} \right) \right)^{-\frac{2\gamma_4}{\gamma_4 - 1}}
\]

- 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

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<th>$\gamma$</th>
<th>$M_1$</th>
<th>$P_2/P_1$</th>
<th>$P_5/P_2$</th>
<th>$T_2/T_1$</th>
<th>$T_5/T_2$</th>
<th>$\rho_2/\rho_1$</th>
<th>$\rho_5/\rho_2$</th>
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<td>50</td>
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<td>4.00</td>
<td>2.50</td>
<td>0.500</td>
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</table>

![Graph showing variation of $P_2/P_1$ and $T_2/T_1$ with $M_s$](image1.png)

![Graph showing variation of $T_5/T_1$ and $T_2/T_1$ with $M_s$](image2.png)
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 ~ 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 $\geq 10$ ms
2. Vibrational Relaxation

Recall our previous lectures on the vibrational energy in diatomic molecules

- Use a simple harmonic oscillator model (HO)

\[ u(r) = \frac{1}{2} k x^2, \quad x = r - r_e = \text{difference in nuclei spacing from equilibrium} \]

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

- But energy levels are quantized!

\[ \varepsilon_i = i\hbar \nu = \text{energy in level } i \]

- Can use Boltzmann statistics (PGD) to determine distribution

\[ x_i^* = \frac{N_i^*}{N} = \frac{e^{\frac{-i\theta_v}{T}}}{1 - e^{\frac{-\theta_v}{T}}} = \text{fractional population in level } i \]

\[ Q = \frac{1}{1 - e^{\frac{-\theta_v}{T}}} \]

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

\[ e_v = \frac{R \theta_v}{e^{\frac{\theta_v}{T}} - 1} = \text{average vibrational energy per molecule} \]
2. Vibrational Relaxation

Vibrational energy distribution function (from Boltzmann statistics)

\[ x_i^* = \frac{N_i^*}{N} = \frac{e^{-i\theta_i/T}}{Q} = \frac{1}{1 - e^{-\theta_i/T}} \]

- 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

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

- \( E_v \) = 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 \( \tau \)?
2. Vibrational Relaxation

Vibrational Relaxation in Shock Tubes

- Test mixture of HO's starts out in vibrational equilibrium (Region 1)
- Translational temperature is instantaneously increased by the arrival of the incident shock
- Vibrational temperature needs time to relax
- V-T energy exchange occurs (and energy must be conserved)
- Faster relaxation time behind reflected shock because temperatures are higher.
- Note the equilibrium temperature is lower than the vibrationally frozen temperature
2. Vibrational Relaxation

Shock Tube Studies of Vibrational Relaxation

- 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

![Experimental data on vibrational relaxation of the components of air.](image)

![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.](image)
2. Vibrational Relaxation

• Modern Experiments with Laser Diagnostics

Goal:
• High-temperature $O_2$ vibration relaxation rates

Experimental Strategy:
• Shock heat highly diluted mixtures of $O_2$ in Ar
• New diagnostic (MIRA laser) to measure $O_2$ in deep UV (Schumann-Runge) at 206 to 245 nm
2. Vibrational Relaxation

ETNA 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 \(O_2\) vibrational populations?
2. Vibrational Relaxation

- **Schumann-Runge O₂ system** \((B^3Σ_u^- \leftarrow X^3Σ_g^+\) 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

![Graph showing vibrational relaxation and absorbances at peak wavelengths.](graph.png)
2. Example O$_2$ Data and Model

- excellent signal-to-noise ratio (noise $\sim$0.3% absorbance)
- High-accuracy determination of $X_{\text{O}_2}$, $T_5$, $P_5$
- high-accuracy measurement of $t_{\text{vib}}$
- Initial data support an evolving Boltzmann distribution for $e_{\text{vib}}$
- $t_{\text{vib}}$ can be plotted on a Landau-Teller plot
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 →
  \[ \tau_{VT}(O₂-O₂) \text{ and } \tau_{VT}(O₂-Ar) \]

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

2. Landau-Teller Plot
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

\[
\begin{align*}
(1) \quad & H_2 + O_2 \longrightarrow HO_2 + H \\
(2) \quad & OH + H_2 \longrightarrow H + H_2O \\
(3) \quad & H + O_2 \longrightarrow OH + O \\
(4) \quad & O + H_2 \longrightarrow OH + H \\
(5) \quad & H + O_2 + M \longrightarrow HO_2 + M \\
(6-8) \quad & H, O, OH + \text{wall} \longrightarrow \text{removal by adsorption, wall-catalyzed reactions \rightarrow stable species}
\end{align*}
\]

Net effect of branching is to create radicals

Step 1: \( H + O_2 \longrightarrow OH + O \)

Step 2: \( OH + H_2 \longrightarrow H + H_2O \)

Step 3: \( O + H_2 \longrightarrow OH + H \)

Step 4: \( OH + H_2 \longrightarrow H + H_2O \)

Net: \( H + O_2 + 3H_2 \longrightarrow 3H + 2H_2O \Rightarrow +2H! \)

- 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 OH*(t) emission at 306 nm (A-X)

- Close agreement of pressure and emission measurement

\[ \tau_{\text{ign}} = 170 \, \mu s \]

**Graph:**
- Pressure [atm] vs. Time [\(\mu s\)]
- OH* emission

**Conditions:**
- 4% H$_2$ / 2% O$_2$ / Ar
- 1124 K, 3.1 atm
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: ~ 1-3 ms test time
- No overlap with RCM operation ~ 10-150 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 (35-45 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

\[
\frac{dP}{dt} = 3\% / \text{ms} \\
\frac{dT}{dt} = 1.2\% / \text{ms}
\]

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

\[
\text{T}_{\text{initial}} = 1039 \text{ K} \\
0.8\% \text{ Propane/ 8\% O}_2/ \text{ Ar}
\]
4.2. Driver inserts for improved spatial and temporal uniformity

- **Result:** \(\frac{dP}{dt} = 0\) prior to ignition
- Improved \(\tau_{\text{ign}}\) for comparison with simulations

- **Solution:** Driver inserts that modify flow to achieve uniform \(P\) and \(T\) 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

- $\frac{dP}{dt} = 0$ data provide improved targets for constant U,V simulations

- Experimentalists must report facility $\frac{dP}{dt}$ 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

- Large reaction volume gives large energy release $\rightarrow \Delta P$ & $\Delta T$
- 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**

![Conventional Shock Tube graph]

- 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: C$_2$H$_4$ Ignition, Temperature and OH

![Temperature and Pressure Diagrams]

- 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 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