Shock Tube/Laser Diagnostics for Fuel and Surrogate Kinetics

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- Advances in Experimental Techniques
- Kinetic Results for Alkanes
- New Directions: Shock Tube Research

Sponsor: AFOSR/USC
Long-Term Program Objectives

- Build an accurate, multi-target, multi-species experimental database for hydrocarbon combustion - *practical fuels and surrogates* - utilizing modern shock tube and laser diagnostic techniques

- Collaboratively develop, evaluate and refine detailed kinetic mechanisms for single-component fuels, multi-component surrogate blends, and practical fuels to establish predictive capabilities for the kinetics of current and future fuels
Advances in Experimental Techniques

Virtues of Shock Tubes and Lasers for Combustion Kinetics:

- Accurately known reaction mixtures and initial conditions, accessibility to wide range of conditions \((P, T)\), wide range of time scales \((\mu s \ to \ ms)\), negligible influence of transport phenomena, ready access for LOS optical diagnostics
- Sensitive, species-specific time-histories via LOS laser absorption diagnostics

Advances in Experimental Techniques:

1. Extension of shock tube test time to access low temperature ignition regime
2. Shock tube geometry modification to maintain constant reaction conditions
3. Development of aerosol shock tube to handle low-vapor-pressure fuels
4. Extension of species detection capabilities to provide time-histories of fuel, intermediate and product species – the holy grail
5. Development of shock tube reactive gasdynamics codes to improve kinetic modeling and extend to post-ignition regime

Work sponsored by ARO and AFOSR
Overview of Stanford Shock Tube Facilities

- Shock Tubes (4 + 1 under construction)
  - Low-Pressure Tubes (15 cm and 14 cm)
  - High-Pressure Tube (5 cm) heatable to 150°C
  - Aerosol Shock Tube (11 cm)
  - Imaging Shock Tube (10 cm sq. under construction)

- Optical Diagnostics
  - Absorption (VUV, UV, Vis, Near-IR, Mid-IR)
  - Kinetic Spectrograph (200-300nm)
  - Emission (UV, Vis, IR)
  - ARAS: H, O, C, N atom detection

- Supporting Equipment
  - Gas Chromatography
  - Excimer Photolysis

- Diagnostics:
  - Gas Chromatograph
  - D2 Lamp
  - PMT
  - ARAS
  - MRAS
  - Ring Dye Laser (UV & Vis)
  - Diode Laser (Near IR & IR)
  - Mid-IR Lasers
  - UV/Vis/IR Emission Detectors
Overview of Laser Absorption Diagnostics for Species Time-History Measurements

### Using Ring Dye/Ar\(^+\) Lasers

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
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<tr>
<td>CH</td>
<td>431</td>
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<tr>
<td>NCO</td>
<td>440</td>
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<tr>
<td>NO(_2)</td>
<td>472</td>
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### With Frequency Doubling

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<td>CH(_3)</td>
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<td>OH</td>
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<tr>
<td>NH</td>
<td>336</td>
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### With Frequency Modulation

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<td>NH(_2)</td>
<td>597</td>
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<td>HCO</td>
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### Using Diode/HeNe Lasers

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<tbody>
<tr>
<td>H(_2)O</td>
<td>1.4</td>
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<tr>
<td>Fuel</td>
<td>3.4</td>
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<tr>
<td>CO</td>
<td>4.6</td>
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<tr>
<td>NO</td>
<td>5.2</td>
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### Recent Additions

<table>
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<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
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<tr>
<td>Benzyl</td>
<td>266</td>
</tr>
<tr>
<td>Toluene</td>
<td>266</td>
</tr>
<tr>
<td>Propargyl</td>
<td>335</td>
</tr>
<tr>
<td>NCN</td>
<td>329</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>244/266</td>
</tr>
<tr>
<td>CO</td>
<td>2.3 µm</td>
</tr>
<tr>
<td>CO(_2), H(_2)O, T</td>
<td>2.7 µm Tunable DFB lasers</td>
</tr>
<tr>
<td>HC Fuels</td>
<td>3.3-3.55 µm Tunable DFG lasers</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>10.5 µm CO(_2) laser</td>
</tr>
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Advances in Experimental Techniques:
1) Extended Test Time in Shock Tubes

Challenge: Longer shock tube test times (> 2 ms) needed for studies at lower temperatures (<900 K) to study NTC regime.

Our Approach: Significant improvements in shock tube test time are possible with:

- Step 1: Driver gas tailoring
  (N$_2$/He driver mix for NTC region)
  ~ 10 ms test time

- Step 2: Driver length change
  (2x driver length)
  ~ 40 ms test time
Application: Extended Shock Tube Test Times Provide Access to Low Temperature n-Heptane Ignition

- New driver length and tailored gas mixtures provide access to long ignition time region
- Strong pressure dependence in NTC region: $t_{\text{ign}} \sim P^{-2}$
- Current models capture trend but not accurate values

- New shock tube data provides targets for model refinement in NTC region
- At long test times must monitor and minimize non-ideal flow variations
Advances in Experimental Techniques:
2) Shock Tube Geometry Modification (Driver Inserts) Alleviate Facility-Related Pressure Variations

**Non-Reactive Case**
- Tailored Driver gas mixture: 50% N₂, 50% He;
- Driven gas: Ar
- Reflected shock conditions: 900 K, 4 atm

- dP/dt (without insert): 1.7%/ms
- dP/dt (with insert): 0%/ms
Application: Resolve ignition time discrepancy in $\text{H}_2/\text{O}_2$ mixtures at low temperatures

- Significant difference seen between conventional shock tube experiments and constant volume models of low-temperature $\text{H}_2/\text{O}_2$ ignition

- Facility effects ($dP/dt$) at long test times in low-temperature shock tube measurements influence ignition times

Strong sensitivity of $\text{H}_2/\text{O}_2$ ignition delay time to pressure and temperature requires improved gasdynamic model for accurate comparison: CHEMSHOCK
Advances in Experimental Techniques: 3) Aerosol Shock Tube

Experimental challenge:

Many practical fuels and propellants have low vapor pressures, requiring heated research facilities to fully vaporize the fuel with the possibility of pre-test fuel decomposition/oxidation

Stanford approach:

- Generate liquid aerosols in shock tube and vaporize behind incident shock
- Provides complete and rapid conversion of fuel to vapor phase without pre-test fuel decomposition/oxidation
- Enables fundamental shock tube studies of practical fuels

*Work on Aerosol Shock Tube (AST) supported by ARO*
Aerosol Shock Tube: 1st Generation

- Fill shock tube with fuel aerosol/oxidizer mixture (3 μm diam. droplets)
- Fully evaporate aerosol behind incident shock wave
  - Confirm evaporation with non-resonant NIR laser extinction
  - Determine fuel loading (and temperature) with 2 color DFG laser
- Measure HC time-histories behind reflected shock waves with DFG laser, radicals with UV laser, products with NIR and MIR TDLs
Aerosol Shock Tube: Complete Conversion to Vapor Behind Shock Waves: n-Dodecane

1. Incident shock arrives
   \(T_2=446\text{ K}, \ P_2=0.78\text{ atm}\)

2. Droplets accelerate and are compressed

3. Droplets evaporate

4. Point of complete conversion to vapor

5. Uniform gas phase formed by diffusion

6. Reflected shock arrives
   \(T_5=618\text{ K}, \ P_5=2.4\text{ atm}\)

- Multi-wavelength diode laser extinction enables determination of droplet size distribution and loading, and confirms complete evaporation \(4\)
- 3.39 \(\mu\)m laser absorption data enables determination of fuel mole fraction before arrival of reflected shock wave at \(5\)
- Next step: study thermal decomposition and oxidation behind reflected shocks in \(6\)
Aerosol shock tube provides access to diesel DF-2 ignition times.

1197 K, 7.2 atm, $\Phi=0.5, 21\%O_2$

- Aerosol shock tube provides first high-concentration ignition time data for diesel (DF-2) with no fuel cracking by mixture heating.
Aerosol Shock Tube: 2nd Generation

**Motivation:** reduce volume of tube filled with aerosol, increase control of fuel loading, improve uniformity

- Use of holding tank for fuel/oxidizer mixture → higher fuel loadings possible, smaller droplets
- Reduced aerosol filling volume in shock tube → reduced contamination of shock tube
- Improved aerosol spatial uniformity by experiment

**Status:** prototype valves and mixture tank are being tested
Advances in Experimental Techniques:
4) Extend Species Detection Capability

Challenge:
- Species time-histories for fuel, intermediate species, and products needed to aid mechanism development and validation

Stanford approach:
- Narrow-linewidth laser absorption provides sensitive, quantitative, *in situ* detection of critical combustion species – *previously we used this primarily for radicals (OH, benzyl, CH, NCN, CH₃ …)*
- New tunable two-color mid-IR detection provides speciation for HC fuels, intermediates and products: n-heptane, n-dodecane, ethylene, propene, methane, propane, CH₂O …
- New tunable mid-IR laser at 2.7 µm provides access to product species CO₂, H₂O, and T
- New tunable CO₂ laser at 10.5 µm for C₂H₄ (applicable to C₃H₆)

*Research on diode laser diagnostics and supporting spectroscopy sponsored by AFOSR*
Stanford’s Novel 2-Color Mid-IR Laser System

- Mid-IR generation uses robust NIR components
- Telecom NIR lasers can tune mid-IR wavelengths $\sim 100 \text{ cm}^{-1}$
- Stanford modification provides two alternating output wavelengths
- Wavelength tunability enables optimization for specific application/species
- Can be used for speciation, for subtraction of droplet/particulate extinction, or for simultaneous species and temperature
Polyatomic Hydrocarbon Fuels Have Strong Mid-IR Absorption, with Some Differences

Hydrocarbon Fuels:
- C-H stretch vibrations have strong absorption strength near 3000 cm\(^{-1}\) (3.3 \(\mu\)m)
- Rotational structure blended into broad features for pure polyatomic hydrocarbon compounds and fuel blends – *but each fuel has different spectrum*
- Can exploit T-dependence of cross-sections to simultaneously measure fuel and T
Fuel Measurements in Heptane Decomposition: Measurement Using Mid-IR Laser Absorption

- Mid-IR laser absorption provides reactant (and product) measurement capability
- Measurements complement direct rate determination using CH₃ laser absorption
- First direct measurements of n-heptane decomposition rate near 1000 K
Advances in Shock Tube Modeling:
5) New Kinetic Code: CHEMSHOCK

- The capability to measure product species (CO$_2$ and H$_2$O) and temperature now enables study of post-ignition phenomena in reflected shock studies.

- But, current constant-volume modeling constraint fails with large energy release after ignition, prohibiting use of species time-histories after ignition, and fails to account for non-ideal facility effects.

- The solution: Development of a new Chemkin-based code CHEMSHOCK enables modeling of 1-D behavior, e.g. due to non-ideal facility effects and energy release, from initial decomposition through ignition to final combustion products.
Use of a New Reflected Shock Code CHEMSHOCK for Reactive Systems with Energy Release

N-Heptane Oxidation

- Pressure, temperature and concentration well modeled using isentropic compression/expansion model for shock tube ignition with energy release
- Allows modeling of 1-D behavior (non-ideal facility effects and energy release)

Initial Conditions:
- 0.2% Heptane/O2/Ar
- 1385 K, 1.4 atm, \( \phi = 1.2 \)
Kinetics Results for Alkanes

- Review of previous high-pressure jet fuel/surrogate ignition time data
- Current program: low-pressure (C5-C9) n-alkane ignition delay time data
- Current program: use of intermediate and high pressure C12 ignition data to test JetSurF mechanism
Review of Jet Fuel and Surrogate Database: High-Pressure Ignition Delay Times

- Heated high-pressure shock tube provides access to smaller alkanes, i.e. <C12
- Aerosol shock tube provides access to larger alkanes, i.e. >C9
- Evidence of NTC behavior below 1000 K in all alkanes and jet fuel

- n-Dodecane and MCH (methylcyclohexane) are potential candidates for high temperature jet fuel surrogate; MCH better for lower temperature (at high P)
Current Program Preliminary Results:
Large N-Alkane Low-Pressure Ignition Survey

Example n-Nonane Data

- High-temperature, low-pressure survey of large n-alkanes to support jet surrogate (dodecane) mechanism development

- First n-nonane ignition delay data: low vapor pressure (~2 torr at 20°C) requires heated shock tube (25°C)
Current Program Preliminary Results: Large N-Alkane Low-Pressure Ignition Survey

- High temperature survey of C5-C9 alkanes shows similar ignition times at 1.5 atm, $\phi=1$
- Agreement with Horning et al. (2002) n-alkane correlation
- Next step: expand $T$, $P$, and mixture range
Current Program High-Pressure n-Dodecane Results: Use of HP data to Test JetSurF Mechanism

20 atm n-Dodecane Ignition

- Heated high-pressure shock tube (HHPST) and aerosol shock tube (AST) provides C12 ignition data

- Current JetSurF mechanism captures trends of high-pressure, low-temperature (NTC) ignition regime for n-dodecane
New Directions for Shock Tube Kinetics Research

- PLIF imaging in shock tube to characterize flow uniformity/non-uniformity behind reflected shock waves

- Accurate temperature measurement using WMS

- Mid-IR laser absorption diagnostics for fuels, intermediates, CO$_2$, H$_2$O and T

- Apply multi-species diagnostics: capability for simultaneous time-histories of up to 6 species and T
Laser Diagnostics for Shock Tube Kinetics Studies

**Issue 1:** Variations of temperature ($T_5$) may be present, under some conditions, potentially impacting kinetics *due to attenuation, curved shocks, shock bifurcation, weak ignition, …*

**Diagnostic Solution:** High-sensitivity PLIF of $T$ and species in new imaging shock tube, combined with new non-reactive and reactive gasdynamic models; sensitive detection of $T(t)$ by TDLAS

**Issue 2:** Ignition delay times alone do not sufficiently test detailed reaction mechanisms

**Diagnostic Solution:** Multi-species time-histories of fuel, radicals, intermediates, products and $T$
OH PLIF Imaging in a Shock Tube: Past Work on Strong and Weak Ignition

- Strong Ignition Limit
  - Highly uniform planar wave observed
  - Imaged Area 27 x 27 mm
  - 1440 K, 1.9 atm, $\phi = 1$
  - $\text{H}_2/\text{O}_2$/90% Ar

- Weak Ignition Limit
  - Slightly non-uniform OH reaction front
  - 1110 K, 1.3 atm, $\phi = 1$
  - $\text{H}_2/\text{O}_2$/90% Ar

- OH PLIF proven for examining inhomogeneities in $\text{H}_2/\text{O}_2$ ignition (McMillin et al. 1990)
- What is needed now: study of non-uniformities in weak ignition limit at longer times
- in non-reacting flows use toluene PLIF for sensitive imaging of $T$
- in reacting flows use PLIF of $\text{OH}$ & $T$ to image spatial variations in reaction progress
New imaging shock tube is under construction

- Toluene strategy offers prospects for <1% imaging of T!
- New reactive gasdynamic modeling effort underway
  - Unsteady 1-D & 2-D with kinetics
  - Bifurcation, curved/oscillating shock, corners, walls, weak ignition, etc.
Use of CO$_2$ laser diagnostic for accurate temperature measurement in shock tubes

- Use of wavelength modulation spectroscopy (2f/1f) can provide accurate (+/- 4 K) determination of reflected shock temperature

- Combined with extended test time techniques and driver inserts can provide ~ 10 ms of high-uniformity test time with 1-L driver, greater than 20 ms with 2-L driver

![Graphs showing temperature and pressure changes over time.](image-url)
Holy Grail of Combustion Kinetics:
Complete Picture of Fuel Chemistry through Multi-Species Time-Histories

CW laser diagnostics can provide time-histories of many species

- Fuel using DFG lasers (3.3-3.5 μm)
- Radicals using UV/Vis lasers (216-614 nm)
- Intermediates using IR strategies (2.3-10.5 μm)
- Products and T using DFB lasers (2.5-2.7 μm)

Fuel & Oxygen
(e.g., n-heptane, n-dodecane)

Initial Decomposition Products

H-Abstraction & Oxidation Products

Intermediate Products

H, OH, H₂, C₂H₄, C₂H₂, CO, CH₂O

Ignition

CO, CO₂, H₂O

Kinetics Shock Tubes
(Dia. = 5, 14, 15, & 15 cm)
Two Species Example: Sensitive Detection of n-Heptane at 3.4 microns and Ethylene at 10.5 microns

- Strong n-heptane absorption at 3.4 $\mu$m accessible with tunable DFG laser; utilize multiple wavelengths to eliminate interference absorptions
- Strong ethylene absorption at 10.53 $\mu$m accessible with tunable CO$_2$ laser (P14 line) with no significant interfering species
- Directly applicable for measuring alkane pyrolysis and oxidation kinetics
Absorption measurements of fuel, stable intermediates and products provide critical decomposition and oxidation information for alkanes and fuel surrogates.

Initial data reveal deficiencies in current detailed mechanisms for heptane.
Current Status of Multi-Species Detection Diagnostics: Capability for Time-Histories of up to 6 species and T

Current Diagnostics

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength</th>
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<tr>
<td>C$_2$H$_4$</td>
<td>10.5 µm</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>3.4 µm</td>
</tr>
<tr>
<td>C$<em>{12}$H$</em>{26}$</td>
<td>3.4 µm</td>
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<tr>
<td>CO$_2$, T</td>
<td>2.7 µm</td>
</tr>
<tr>
<td>OH</td>
<td>306 nm</td>
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<tr>
<td>H$_2$O, T</td>
<td>2.5 µm</td>
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Next Species Targets:

- **Fuels**: methylcyclohexane, JP- and RP-fuels
- **Radical Species**: CH$_3$, C$_3$H$_3$
- **Stable Intermediates**: Butadiene, propene, CH$_2$O
- **Products**: CO, NO, Soot
Key Accomplishments and Future Work

- Development and application of advanced shock tube/lasers techniques:
  - Extended test time x10 and improved uniformity of reaction conditions
  - Developed aerosol shock tube for low-vapor-pressure fuel
  - Extended detection capability to hydrocarbons, products and T
  - Developed initial modeling capability for facility effects and energy release

- Database Development: Ignition times
  - High-pressure Jet fuel and major surrogate components
  - Low-pressure C5-C9 n-alkanes and mid-pressure C12

- Future Work:
  - Extend ignition time data to wider T and P regimes and larger alkanes
  - Accurate T measurement using WMS
  - Multi-species time-histories
  - Interact with model developers to design/execute optimized experiments
  - Direct elementary reaction studies