Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

JUNE 25-29, 2018

15 Lecture Short Course at Princeton University

Lecturer: Ronald K. Hanson

Woodard Professor, Dept. of Mechanical Engineering
Stanford University

Underlying Science:
Molecular Spectroscopy
Diagnostic Methods:
Laser Absorption, LIF
Example Applications:
Engines, Shock Tubes, Kinetics

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Today/Lecture 1:
- **Overview**
- **Introductory Material**

Lecture 1: Course Overview

Course Objectives and Content

- Introduction to fundamentals of molecular spectroscopy & photo-physics
- Introduction to laser absorption and laser-induced fluorescence
- Introduction to shock tubes as a primary tool for studying combustion chemistry, including recent advances and kinetics applications
- Example laser diagnostic applications including:
  - multi-parameter sensing in different types of propulsion flows and engines
  - species-specific sensing for shock tube kinetics studies
  - PLIF imaging in high-speed flows

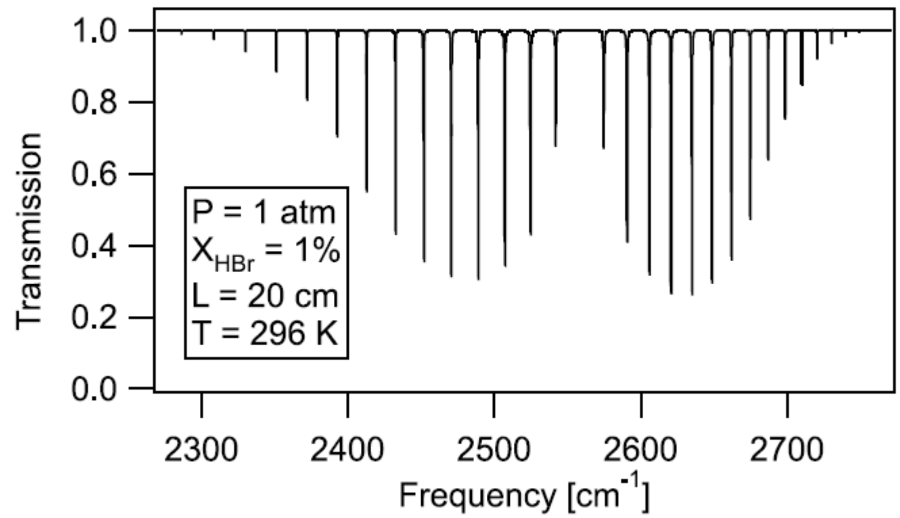
Next: Spectroscopy and Roles of Lasers

Course Overview: Spectroscopy and Lasers

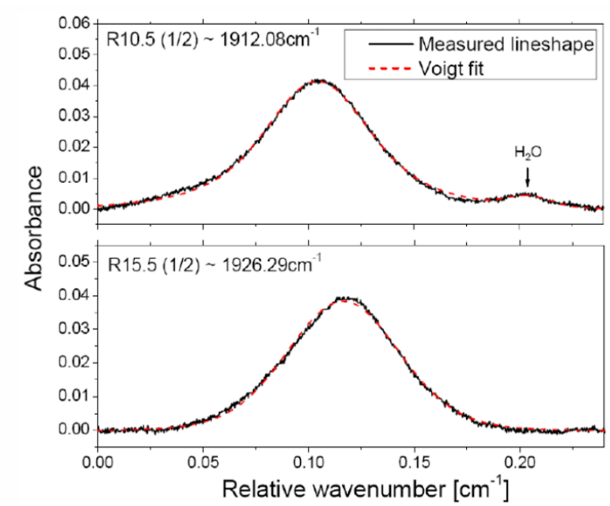
- *What is Spectroscopy?*
  - Interaction of Radiation (Light) with Matter (in our case, Gases)
  - Examples: IR Absorption

- *Why Lasers?*
  - Enables Important Diagnostic Methods
  - LIF, Raman, LII, PIV, CARS, …
  - Our Emphasis: Absorption and LIF
  - Why: Sensitive and Quantitative!

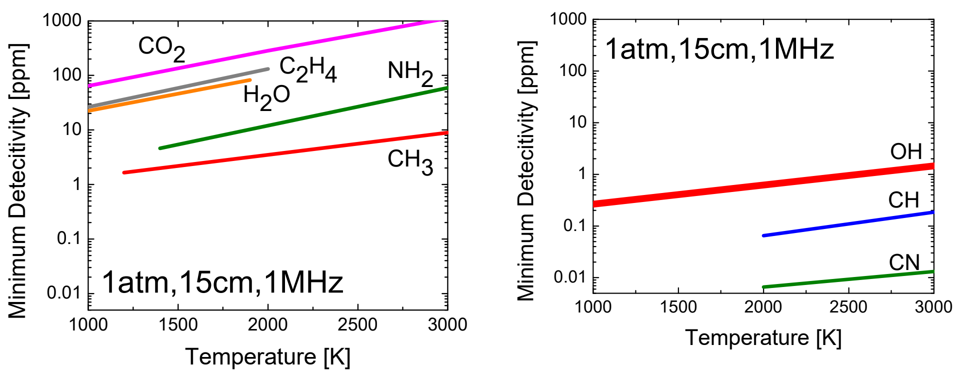
Calculated IR absorption spectra of HBr



Spectrally resolved individual absorption line of NO at 600 K, 1 atm (in C2H4 combustion exhaust)



Minimum Detectivity using Laser Absorption

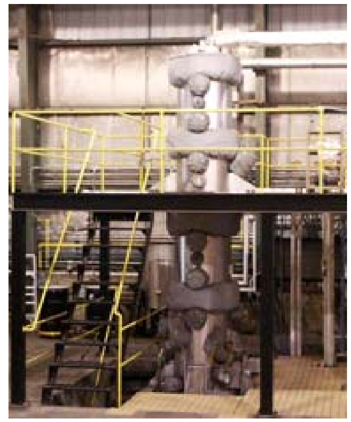


Course Overview:
Role of Lasers in Energy Sciences

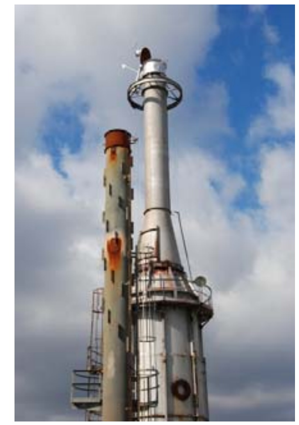
- *Example Applications:*
  Remote sensing, combustion and gasdynamic diagnostics, process control, energy systems and environmental monitoring.

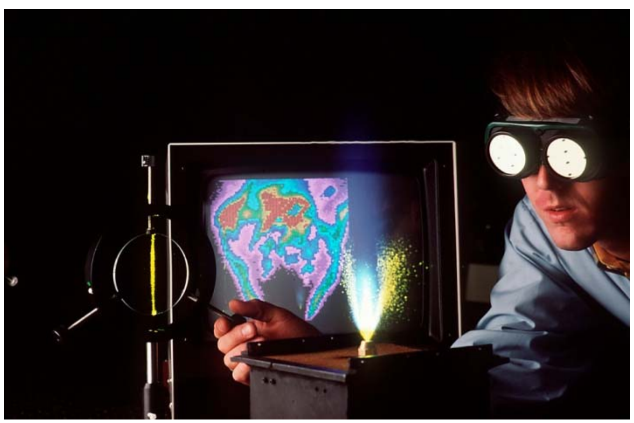
- *Common Measurements:*
  Species concentrations, temperature (T), pressure (P), density (ρ), velocity (u), mass flux (ρu).

Coal gasifiers



Swirl burners





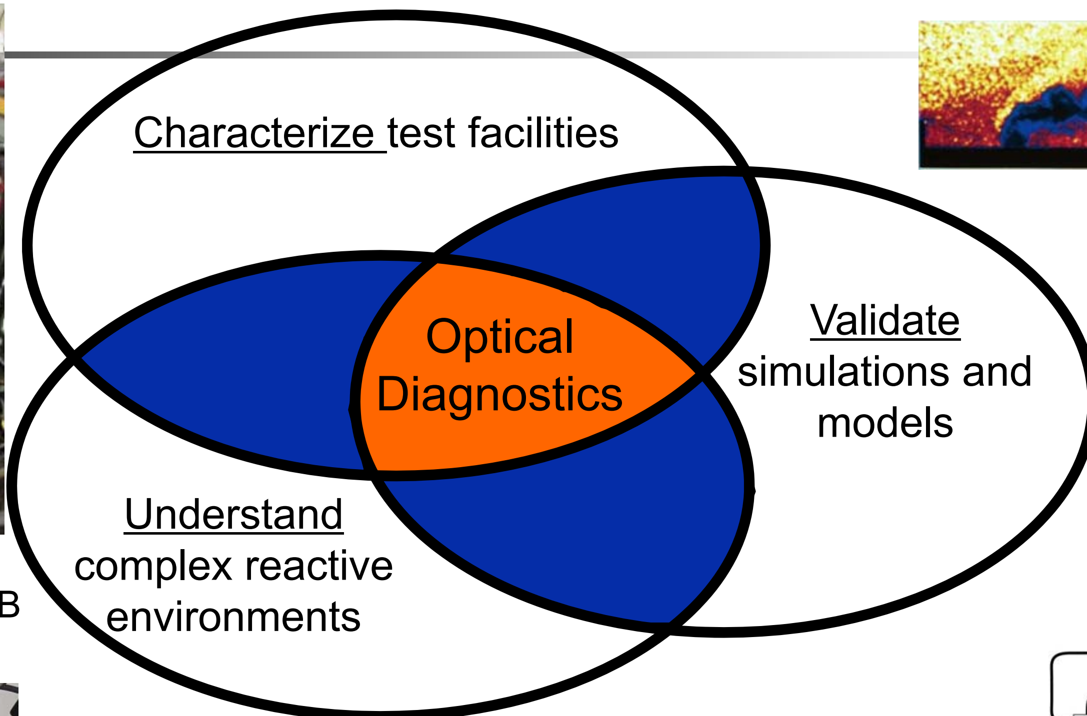
OH PLIF in spray flame

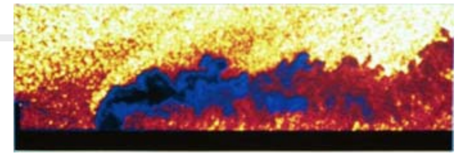
Coal-fired power plants

Incinerators

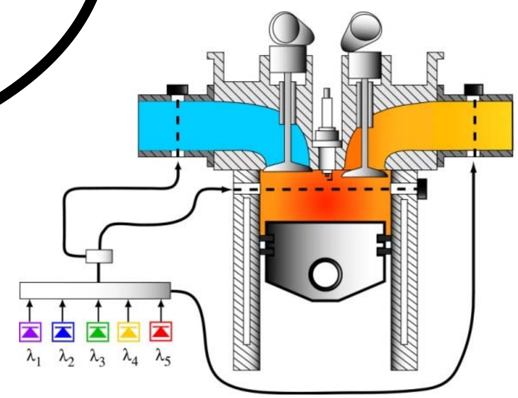
Course Overview: Roles of Laser Sensing for Propulsion

TDL Sensing in SCRAMJET @ WPAFB

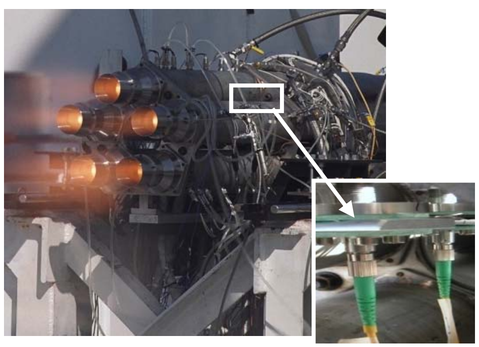




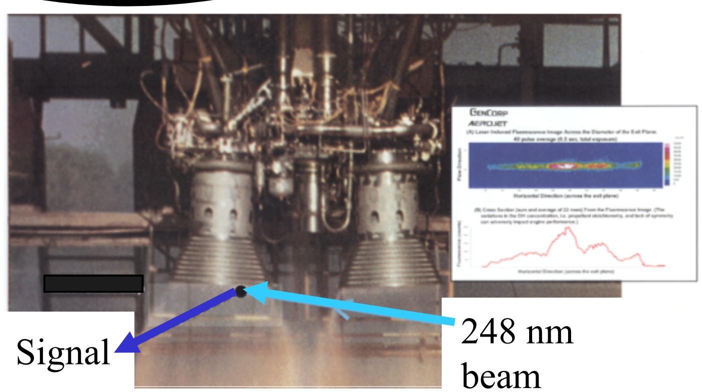
PLIF imaging of H_2 jet in model SCRAMJET @Stanford



TDL Sensing in IC-Engines @ Nissan & Sandia



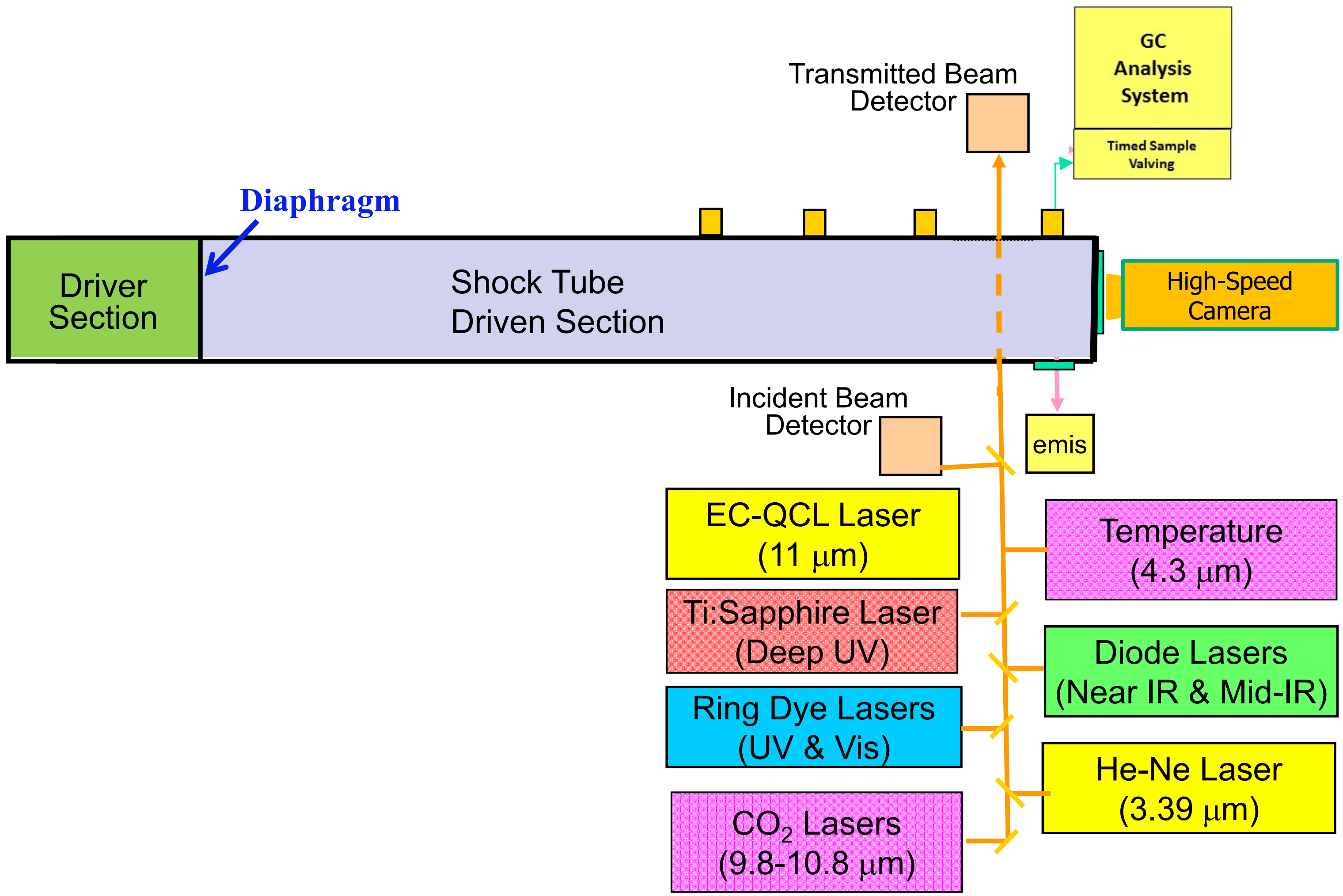
TDL Sensing in Pratt & Whitney PDE @ China Lake, CA



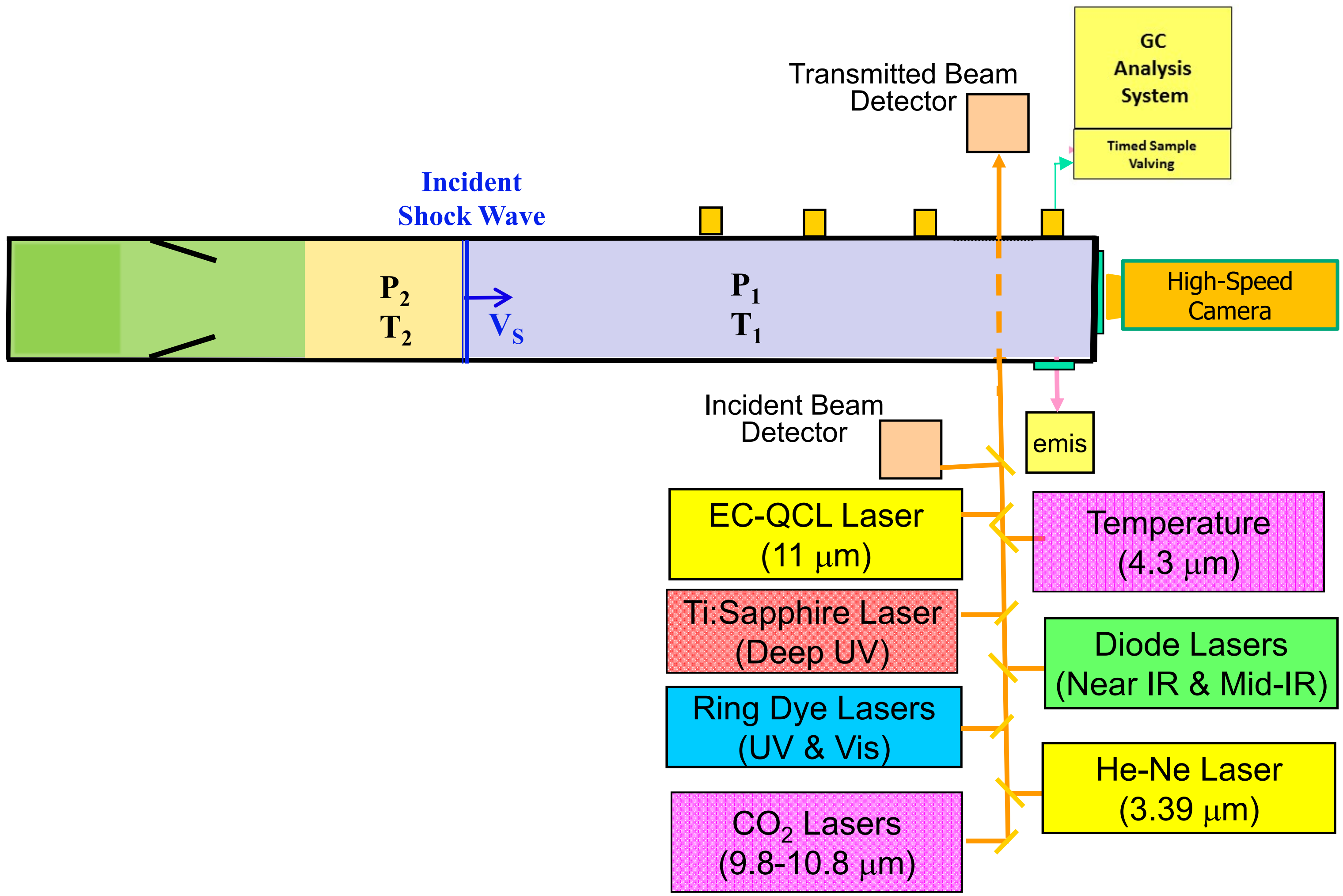
PLIF in plume of Titan IV @ Aerojet

Applicable to large-scale systems as well as laboratory science

Course Overview:
Role of Lasers in Combustion Kinetics: Shock Tubes



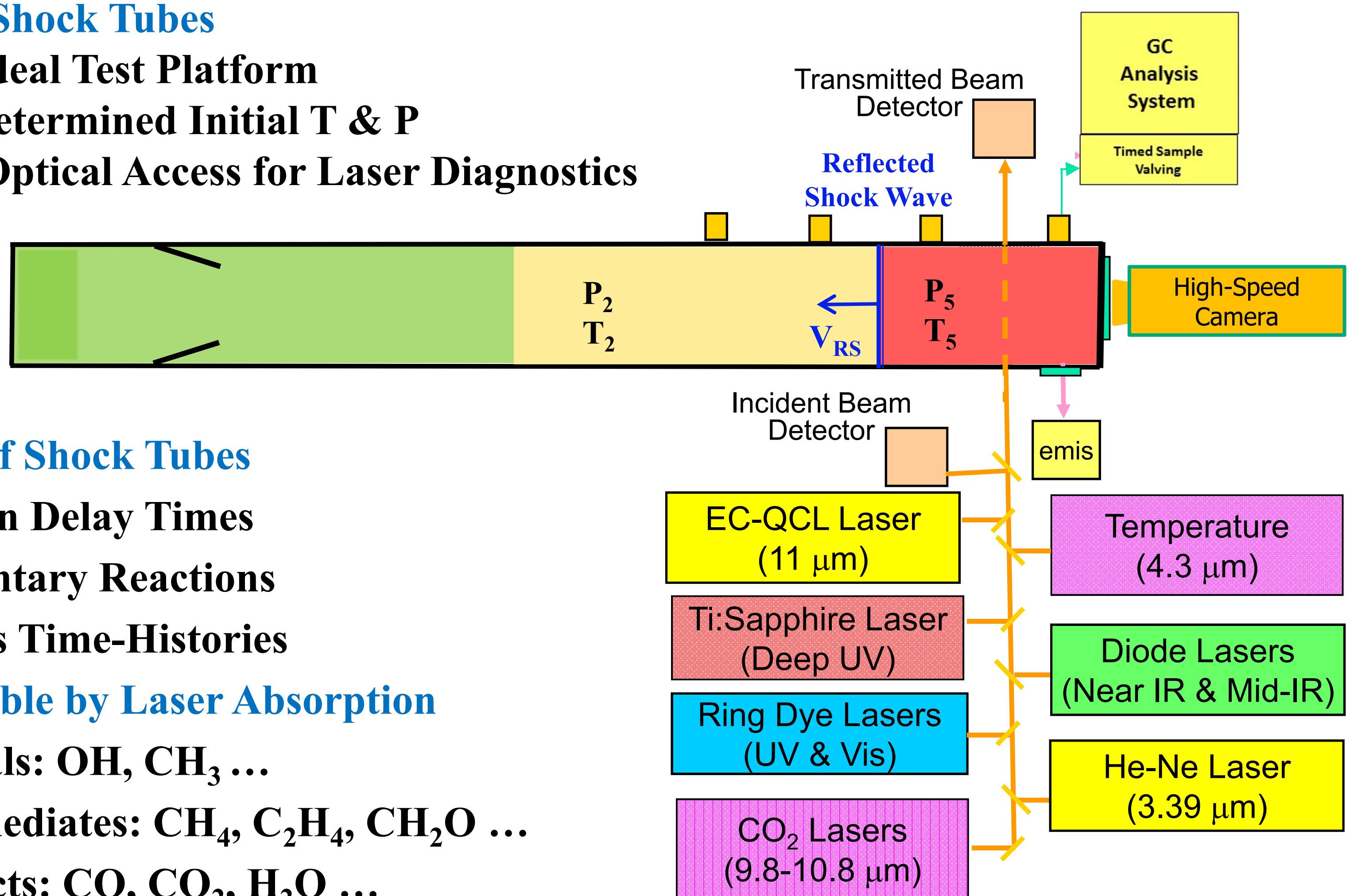
Course Overview:
Role of Lasers in Combustion Kinetics: Shock Tubes



Course Overview:
Role of Lasers in Combustion Kinetics: Shock Tubes

Advantages of Shock Tubes

- Near-Ideal Test Platform
- Well-Determined Initial T & P
- Clear Optical Access for Laser Diagnostics



Applications of Shock Tubes

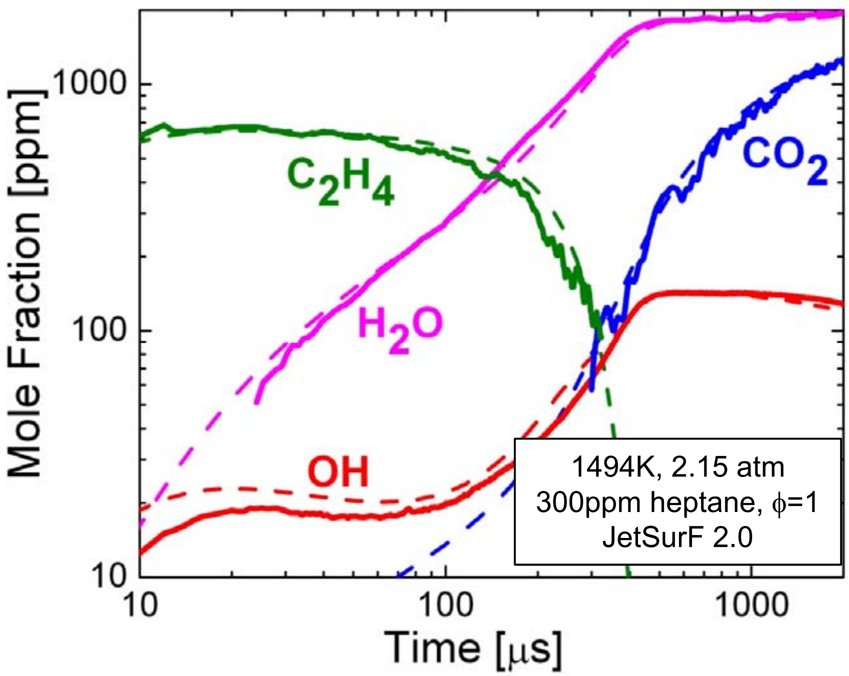
- Ignition Delay Times
- Elementary Reactions
- Species Time-Histories

Species Accessible by Laser Absorption

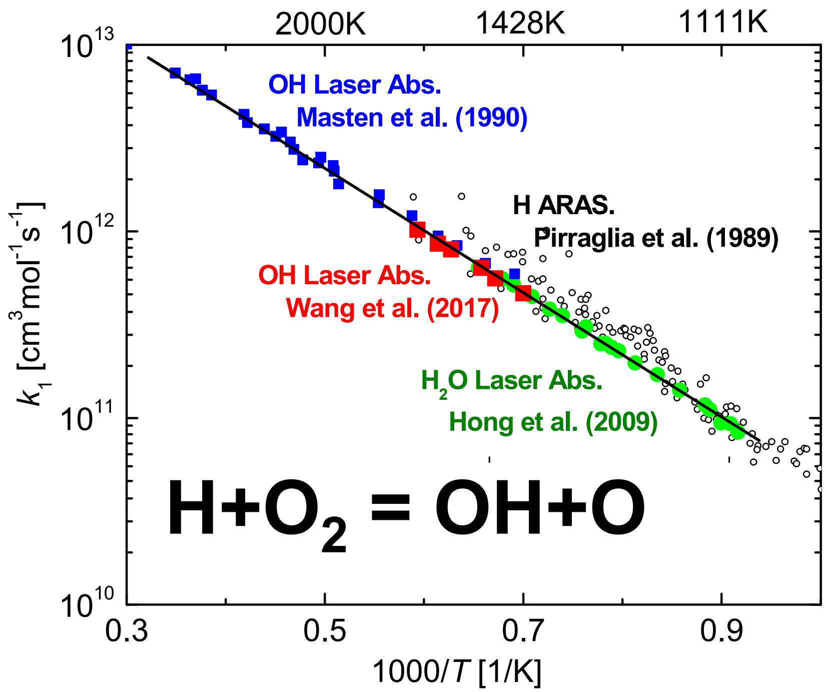
- Radicals: OH, CH_3 …
- Intermediates: CH_4, C_2H_4, CH_2O …
- Products: CO, CO_2, H_2O …

Course Overview:
Lasers and Shock Tube: Time-Histories & Kinetics

Time-Histories



Rate Constant



- Multi-wavelength laser absorption species time-histories provide quantitative targets for model refinement and validation
- Laser absorption provides high-accuracy measurements of elementary reaction rate constants

Useful Texts, Supplementary Reading

- G. Herzberg, Atomic spectra and atomic structure, 1944.
- G. Herzberg, Spectra of diatomic molecules, 1950.
- G. Herzberg, Molecular spectra and molecular structure, volume II, Infrared and Raman Spectra of Polyatomic Molecules, 1945.
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- C.N. Banwell and E.M. McCash, Fundamentals of molecular spectroscopy, 1994.
- S.S. Penner, Quantitative molecular spectroscopy and gas emissivities, 1959.
- A.C.G. Mitchell and M.W.Zemansky, Resonance radiation and excited atoms, 1971.
- C.H. Townes and A.L. Schawlow, Microwave spectroscopy, 1975.
- M. Diem, Introduction to modern vibrational spectroscopy, 1993.

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- A.C. Eckbreth, Laser diagnostics for combustion temperature and species, 1988.
- W. Demtroder, Laser spectroscopy: basic concepts and instrumentation, 1996.
- R.W. Waynant and M.N. Ediger, Electro-optics handbook, 2000.
- J.T. Luxon and D.E.Parker, Industrial lasers and their applications, 1992.
- J.Hecht, Understanding lasers: An entry level guide, 1994.
- K.J.Kuhn, Laser engineering, 1998.
- R.K. Hanson et al., Spectroscopy and Laser Diagnostics for Gases, 2016

Lecture Schedule

Monday

1. Overview & Introduction
Course Organization, Role of Quantum Mechanics,
Planck's Law, Beer's Law, Boltzmann distribution
2. Diatomic Molecular Spectra
Rotational Spectra (Microwaves)
Vibration-Rotation (Rovibrational) Spectra (Infrared)
3. Diatomic Molecular Spectra
Electronic (Rovibronic) Spectra (UV, Visible)

Tuesday

4. Polyatomic Molecular Spectra
Rotational Spectra (Microwaves)
Vibrational Bands, Rovibrational Spectra
5. Quantitative Emission/ Absorption
Spectral absorptivity, Eqn. of Radiative Transfer
Einstein Coefficients/Theory, Line Strength
6. Spectral Lineshapes
Doppler, Natural, Collisional and Stark broadening,
Voigt profiles

Wednesday

7. Electronic Spectra of Diatomics
Term Symbols, Molecular Models: Rigid Rotor,
Symmetric Top, Hund's Cases, Quantitative Absorption
8. Case Studies of Molecular Spectra
Ultraviolet: OH
9. TDLAS, Lasers and Fibers
Fundamentals and Applications in Aeropropulsion

Thursday

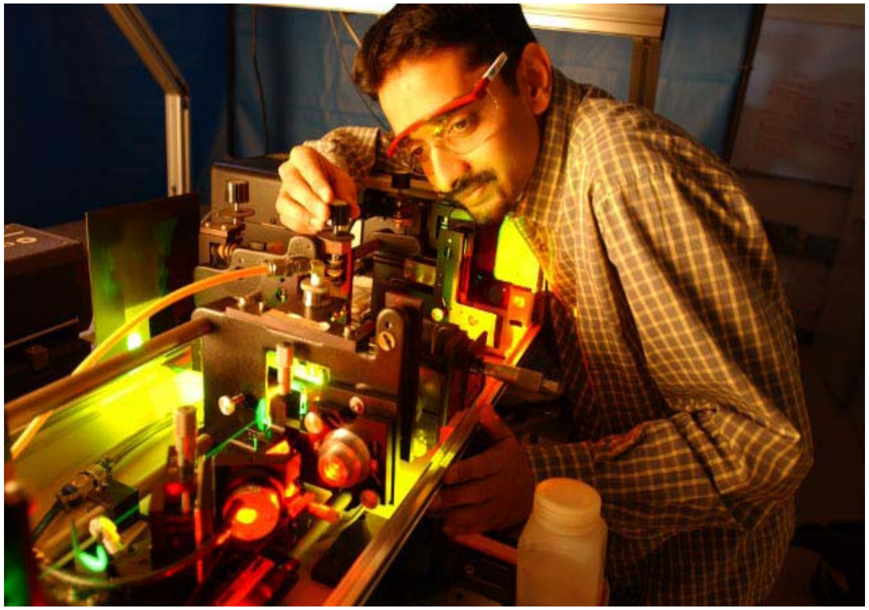
10. TDLAS Applications in Energy Conversion
Tunable Diode Laser Applications in IC Engines
Coal-Fired Combustion
11. Shock Tube Techniques
What is a Shock Tube?
Recent Advances, ignition Delay Times
12. Shock Tube Applications
Multi-Species Time Histories
Elementary Reactions

Friday

13. Laser-Induced Fluorescence (LIF)
Two-Level Model
More Complex Models
14. Laser-Induced Fluorescence: Applications 1
Diagnostic Applications (T, V, Species)
PLIF for small molecules
15. Laser-Induced Fluorescence: Applications 2
Diagnostic Applications & PLIF for large molecules
The Future

Lecture 1: Introductory Material

1. Role of Quantum Mechanics
   - Planck's Law
2. Absorption and Emission
3. Boltzmann Distribution
4. Working Examples



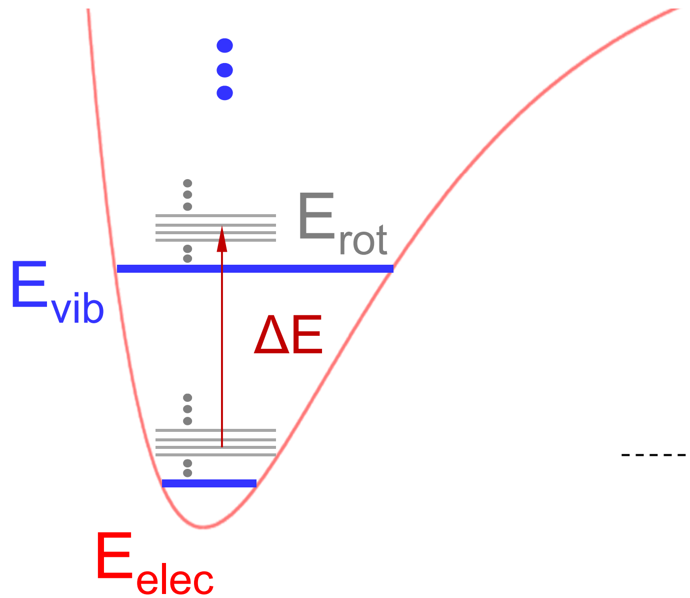
1. Role of QM - Planck's Law

- Quantum Mechanics:
  - Quantized Energy levels
  - "Allowed" transitions

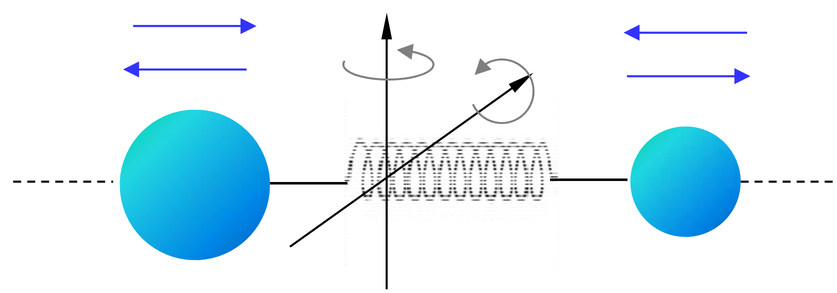
} We will simply accept these rules from QM

How are energy levels specified?

Quantum numbers for electronic, vibrational and rotational states.



$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$

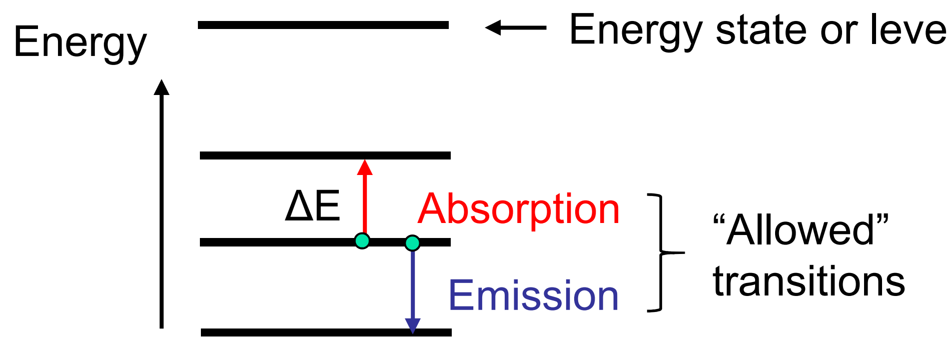


1. Role of QM - Planck's Law

- Quantum Mechanics

Quantized Energy States (discrete energy levels)

Discrete spectra



- Small species, (e.g., NO, CO, CO_2, and H_2O), have **discrete** spectral features
- Large molecules (e.g., HCs) have **blended** features

Planck's Law:

$\Delta E = E_{upper}\,(E') - E_{lower}\,(E'')$
$= h\nu$
$= hc/\lambda$
$= hc\bar{\nu}$ ← Energy in wavenumbers

$c = \lambda\,\nu$

Frequency [s^{-1}]

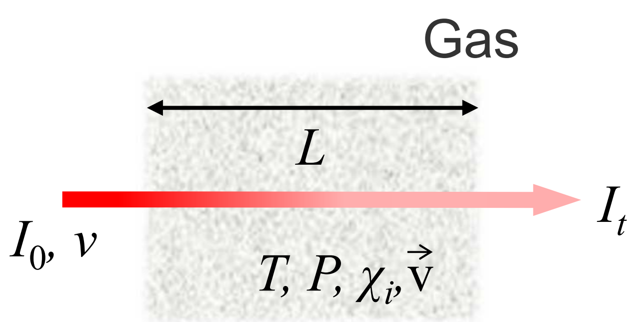
~ 3×10^{10} cm/s   Wavelength [cm]

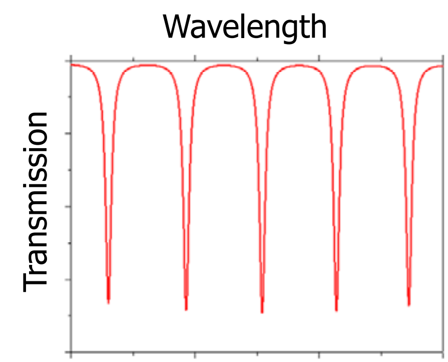
Note interchangability of λ & ν

2. Absorption and Emission

- Types of spectra:
  - Absorption; Emission; Fluorescence; Scattering (Rayleigh, Raman)

- Absorption: Governed by Beer's Law





Absorbance

Beer-Lambert Law $\left(\frac{I_t}{I_0}\right)_\lambda = T_\lambda = \exp(-\alpha) = \exp(-n_j \sigma L) = \exp(-S P \chi_i \varphi L)$

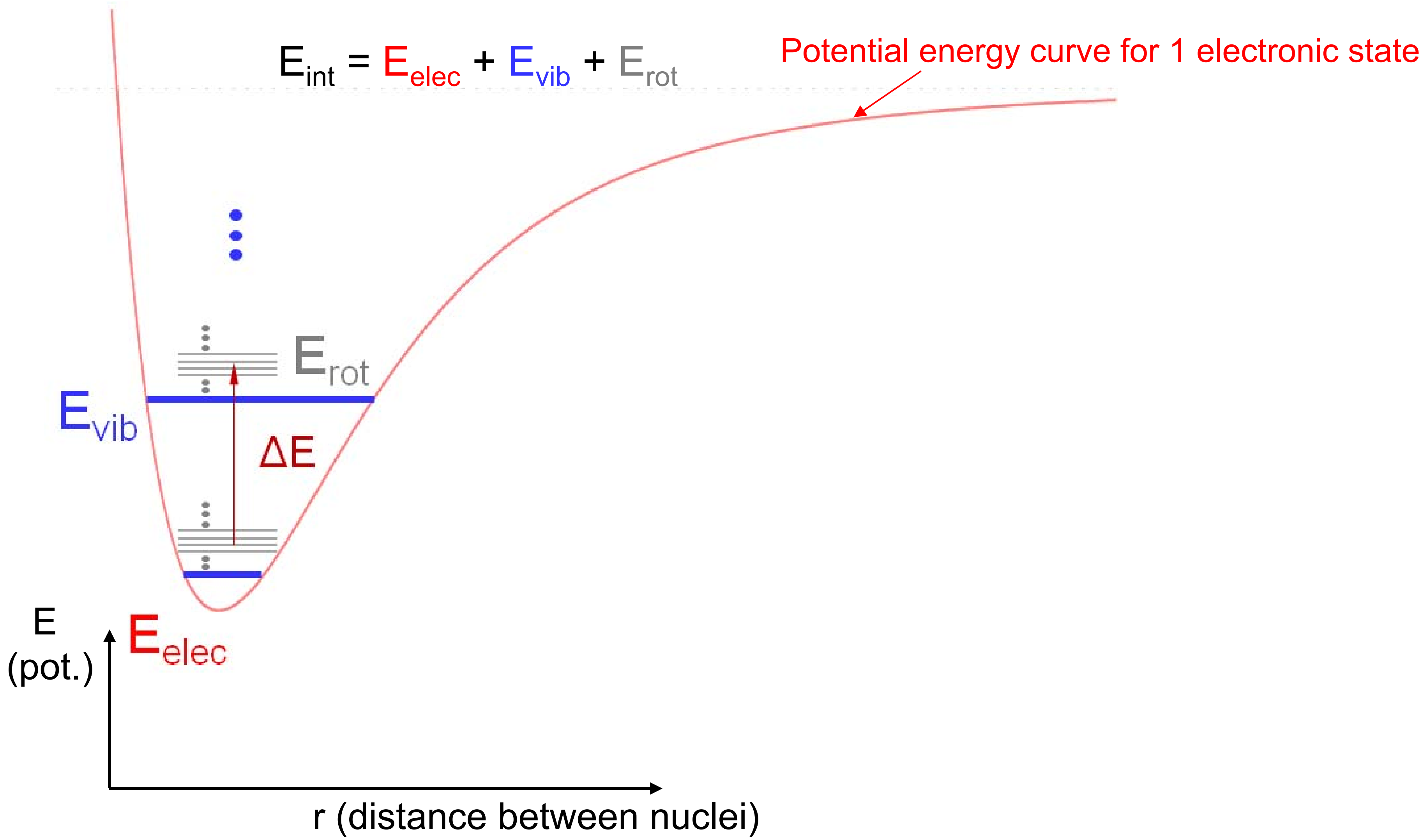
Number density of species j in absorbing state [molecule/cm^3]

Cross section for absorption [cm^2/molecule]

Path length [cm]

2. Absorption and Emission

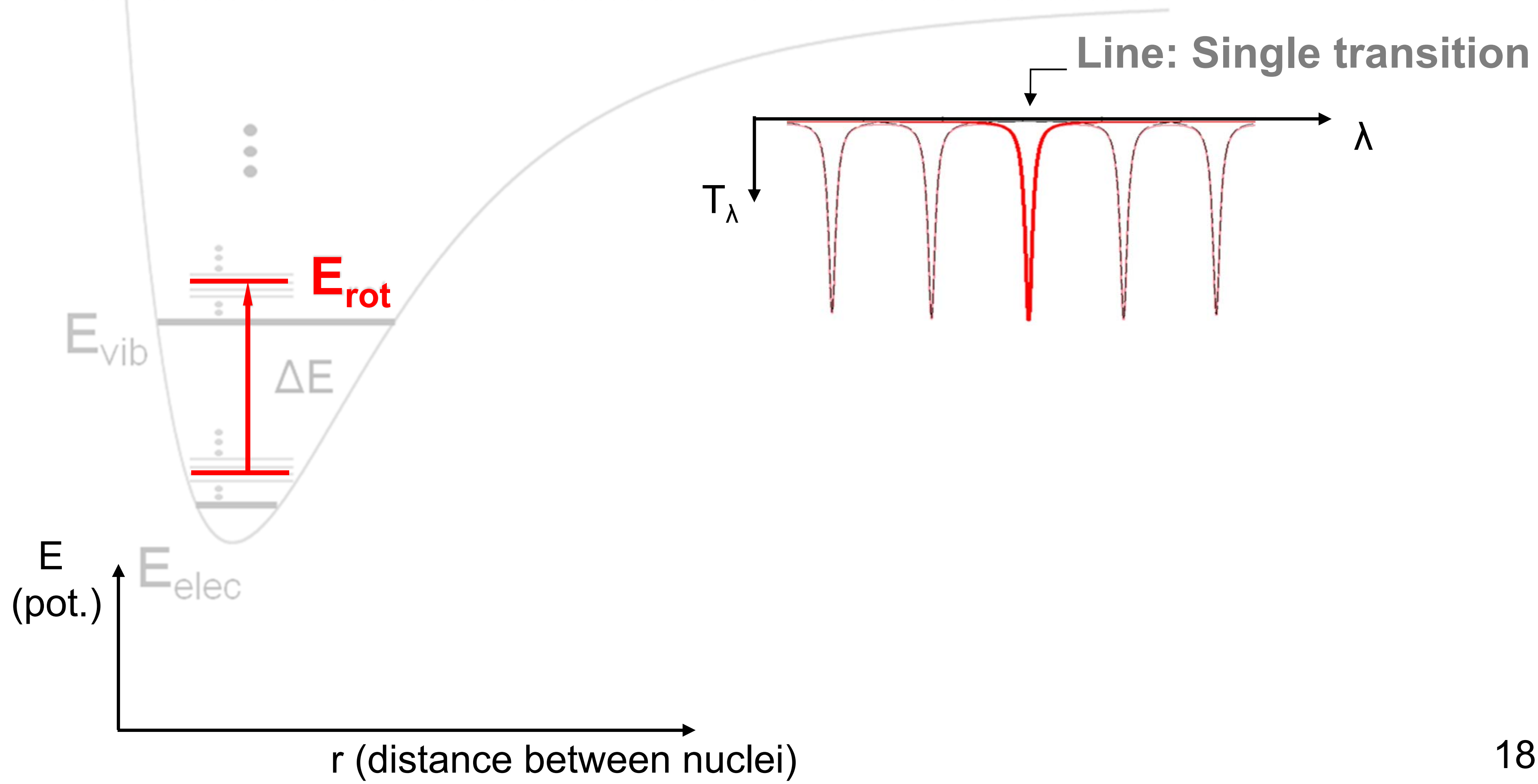
- Components of spectra: Lines, Bands, Systems



2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems

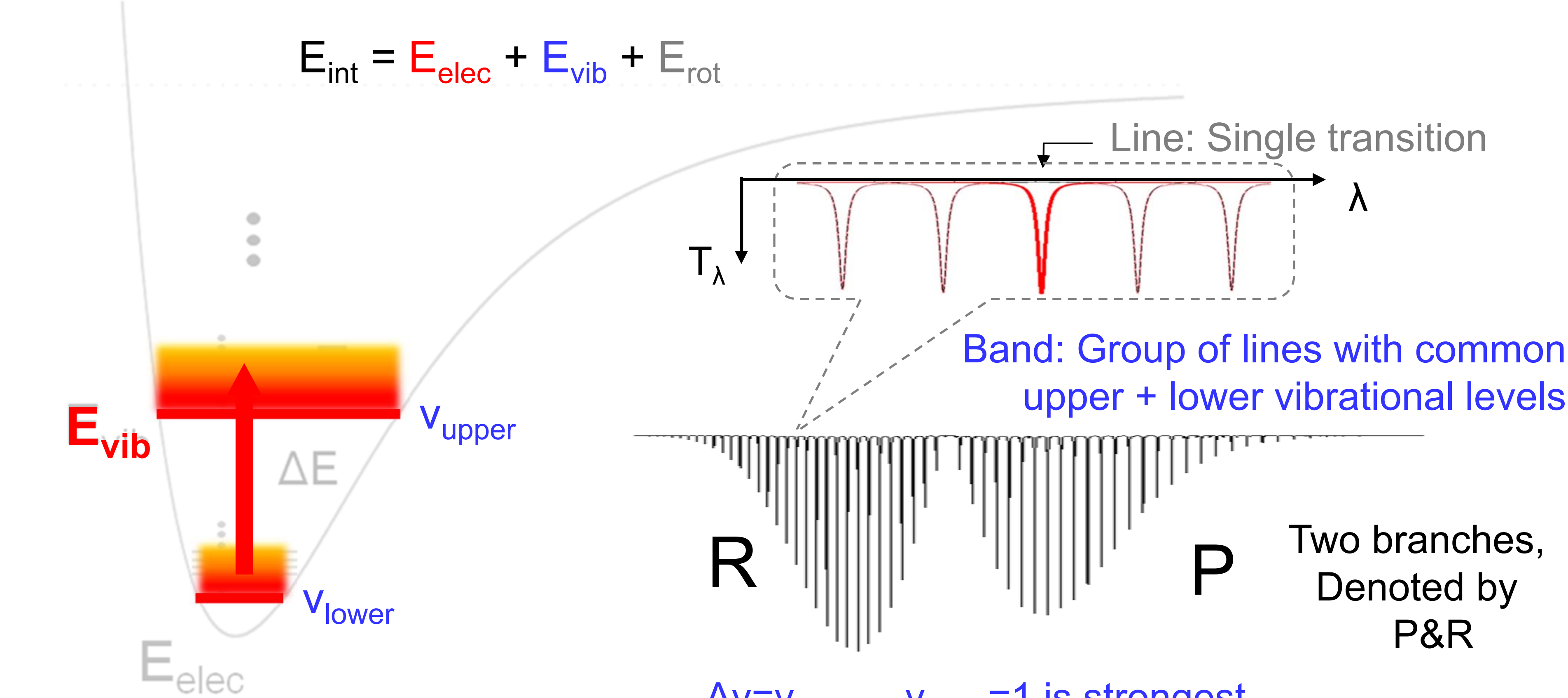
$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$



2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems

$E_{int} = E_{elec} + E_{vib} + E_{rot}$

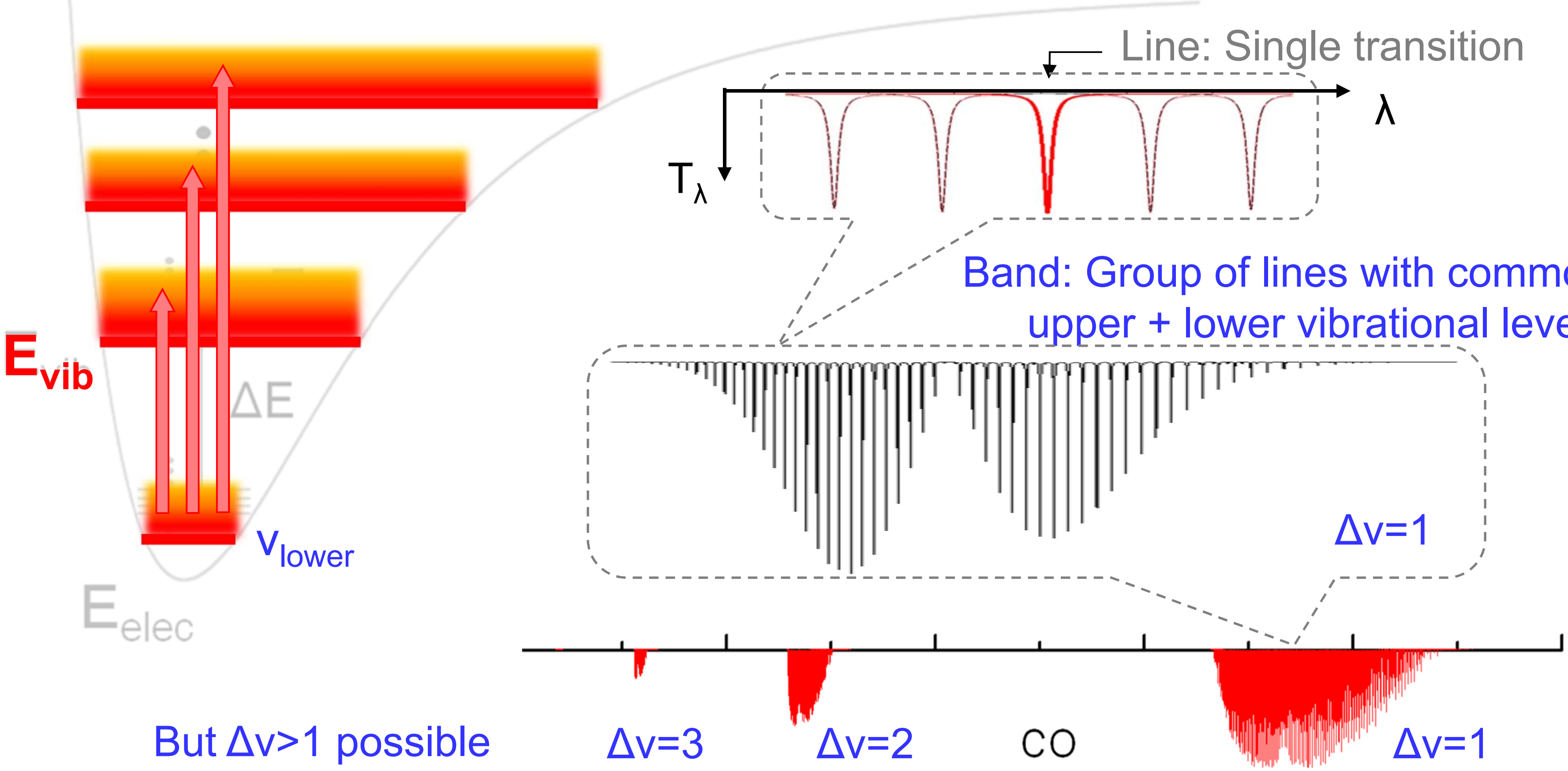


$\Delta v = v_{upper} - v_{lower} = 1$ is strongest for rovibrational IR spectra, but $\Delta v = 2, 3, \ldots$ allowed

2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems

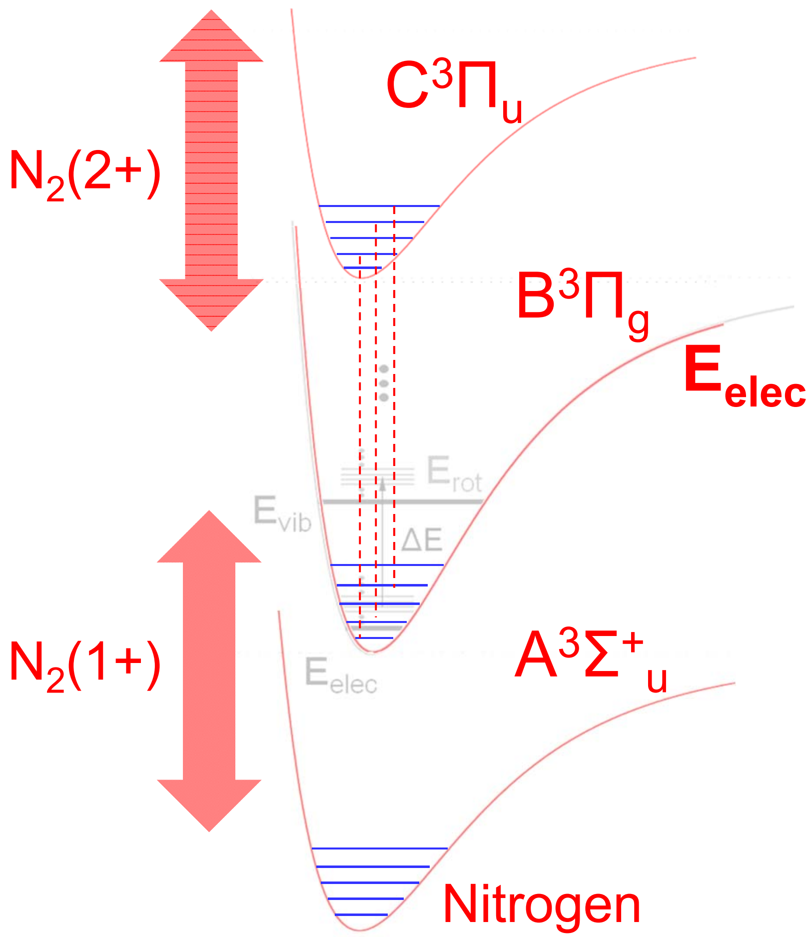
$E_{int} = E_{elec} + E_{vib} + E_{rot}$



2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems

$E_{int} = E_{elec} + E_{vib} + E_{rot}$



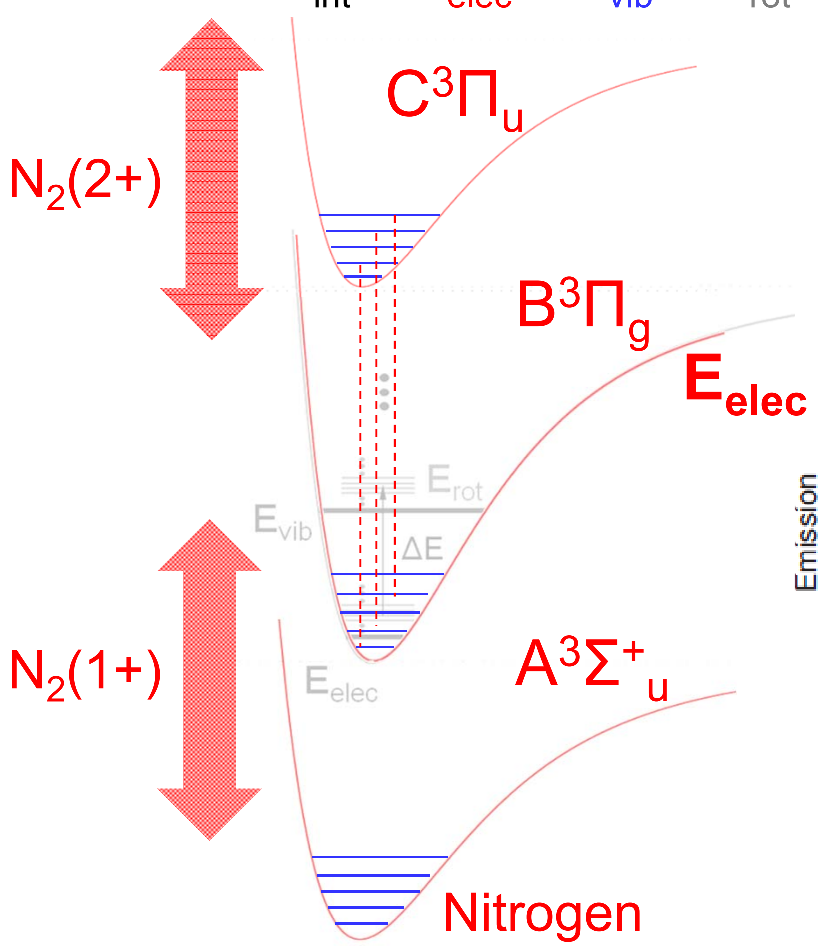
System:
- Transitions between different electronic states
- Comprised of multiple bands between two electronic states
- Different combinations of v_{upper} and v_{lower} such that "bands" with v_{upper}-v_{lower}=const. appear

Example: N_2
- First positive SYSTEM: $B^3\Pi_g \rightarrow A^3\Sigma^+_u$
- The ground (lowest energy) state is $X^1\Sigma^+_g$

2. Absorption and Emission

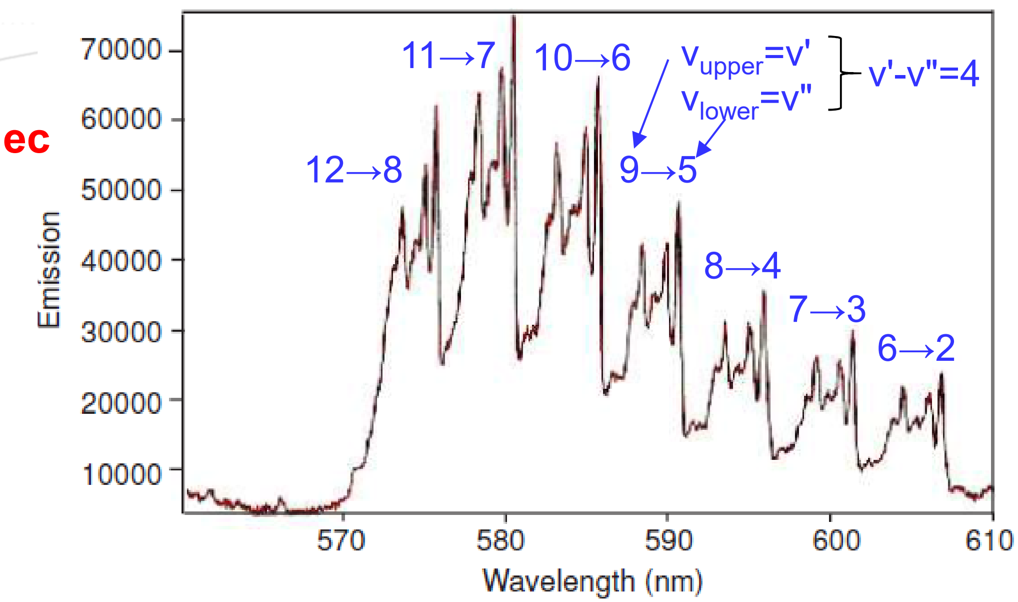
- Components of spectra: Lines, Bands, Systems

$E_{int} = E_{elec} + E_{vib} + E_{rot}$



System

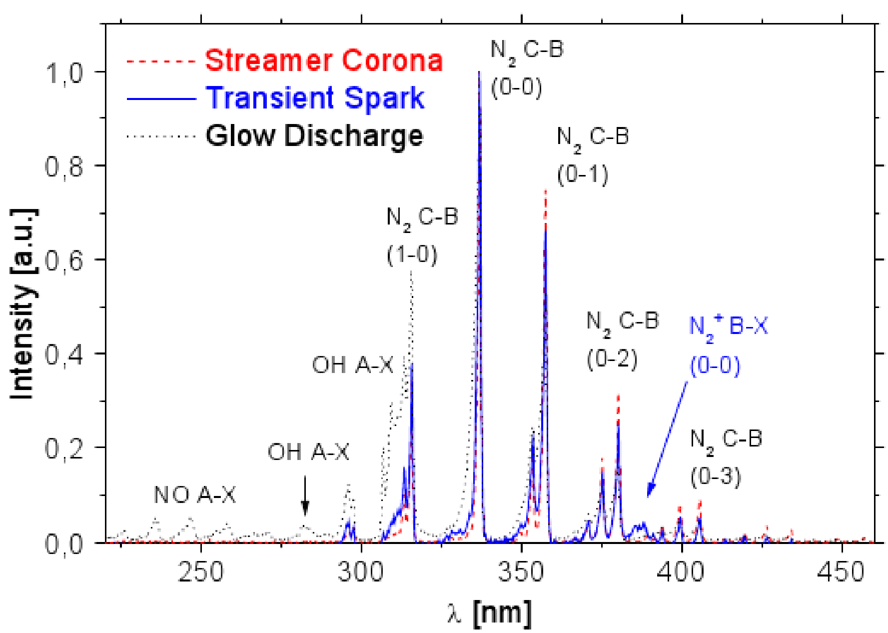
Example: High-temperature air emission spectra (560-610nm)



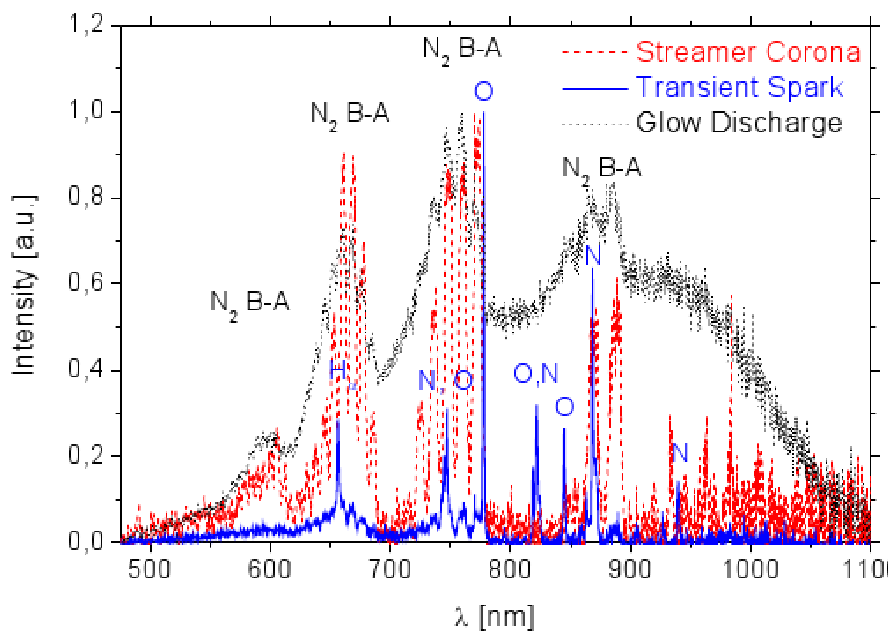
2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems

System
Example: Typical emission spectra of DC discharges



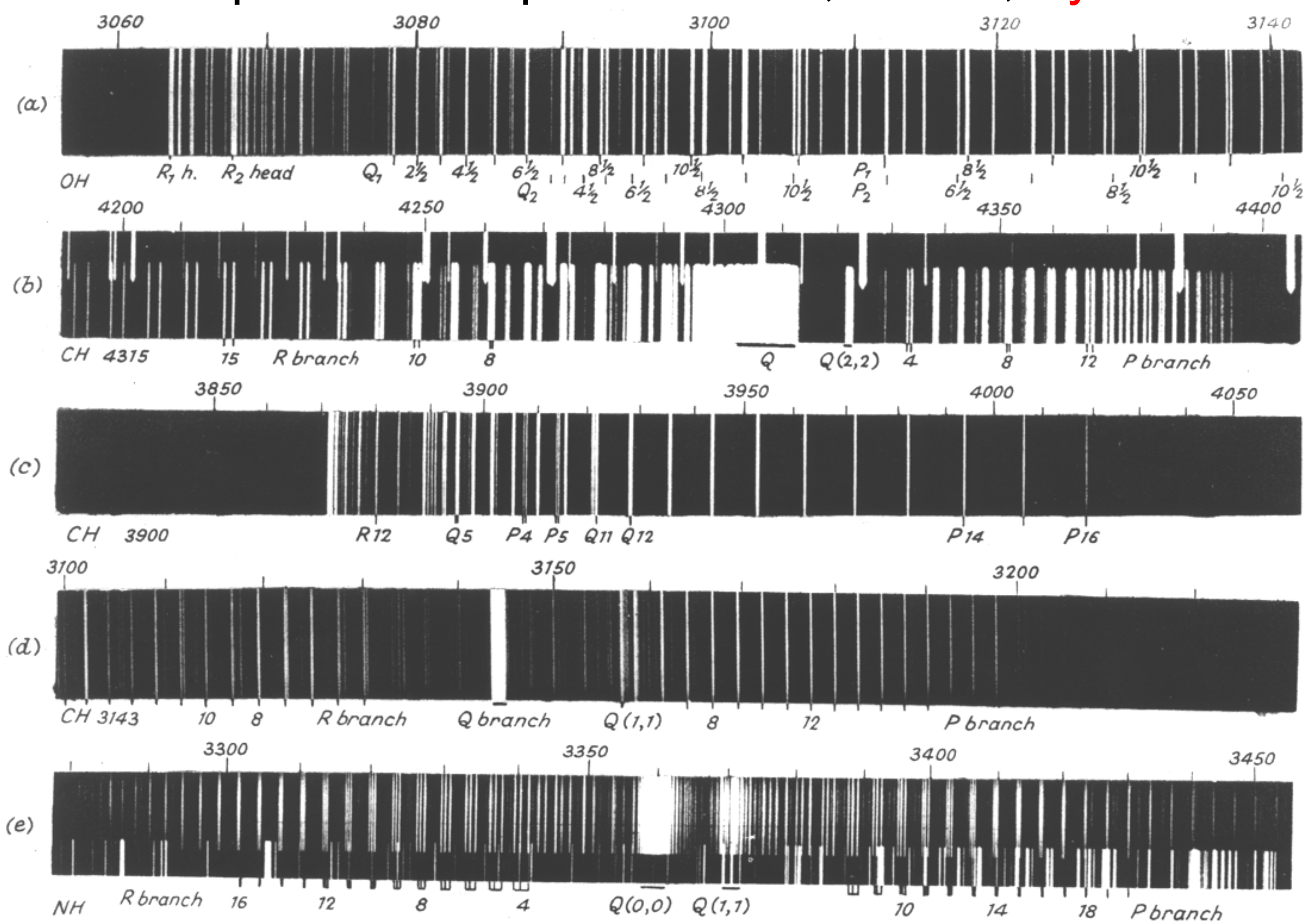
UV



Visible-NIR

2. Absorption and Emission

- Components of spectra: Lines, Bands, Systems



OH $^2\Sigma - ^2\Pi$ (0,0)

CH $^2\Delta - ^2\Pi$

CH $^2\Sigma - ^2\Pi$

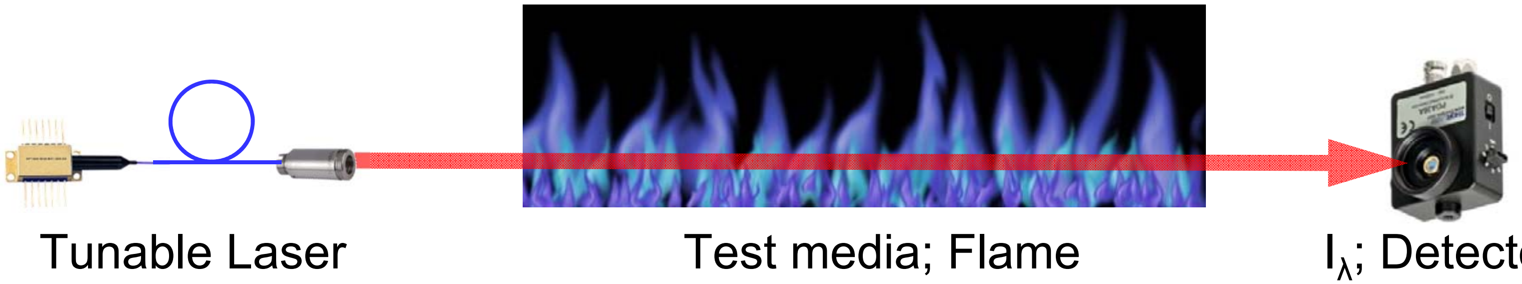
CH $^2\Sigma - ^2\Pi$

NH $^3\Pi - ^3\Sigma$

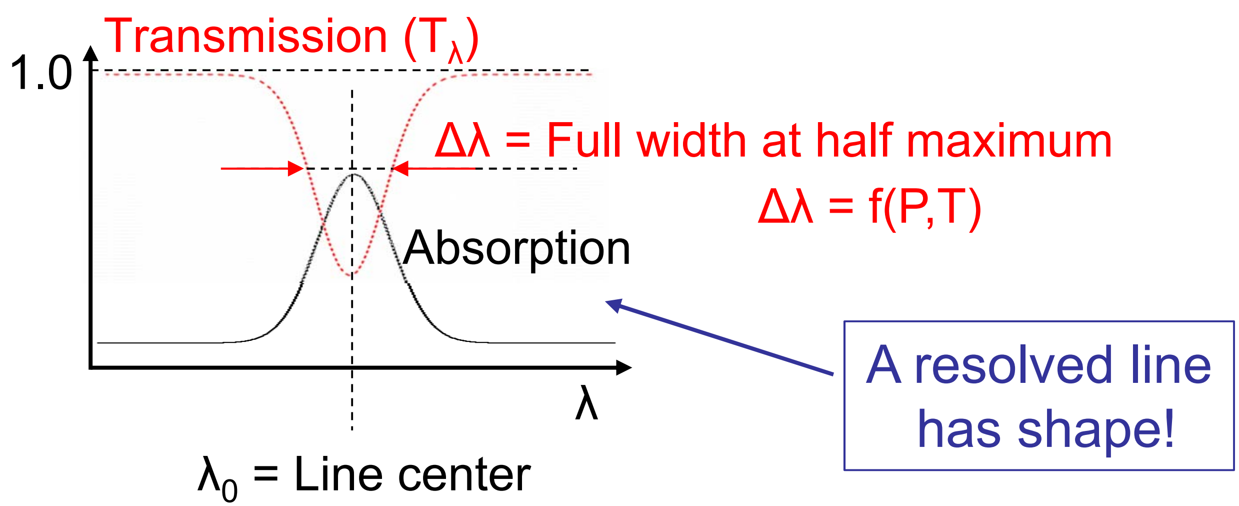
- In early days, spectra were recorded on film!
  But now we have lasers.

2. Absorption and Emission

- How is T_λ (fractional transmission) measured?



- Do lines have finite width/shape? Yes!



And shape is a f(T,P) → an opportunity for diagnostics!

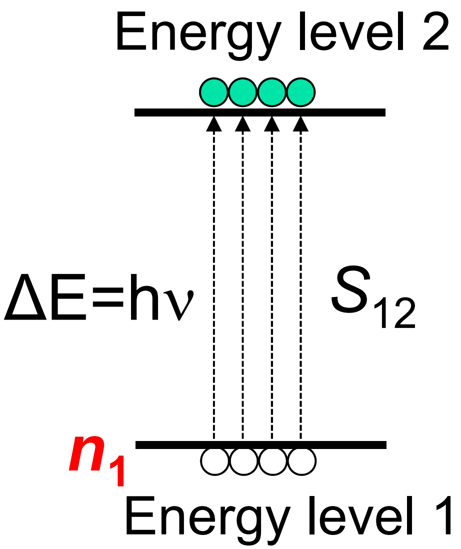
2. Absorption and Emission

- 3 key elements of spectra
  - Line positions
  - Line strengths
  - Line shapes

Covered in course

3. Boltzmann Distribution

- **How strong is a transition?** ⇨ Proportional to particle population in initial energy level n_1



Boltzmann fraction of absorber species *i* in level 1

$$F_i = \frac{n_i}{n} = \frac{g_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}{Q}$$

- Equilibrium distribution of molecules of a single species over its allowed quantum states.

Partition function $Q = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) = Q_{rot} Q_{vib} Q_{elec}$

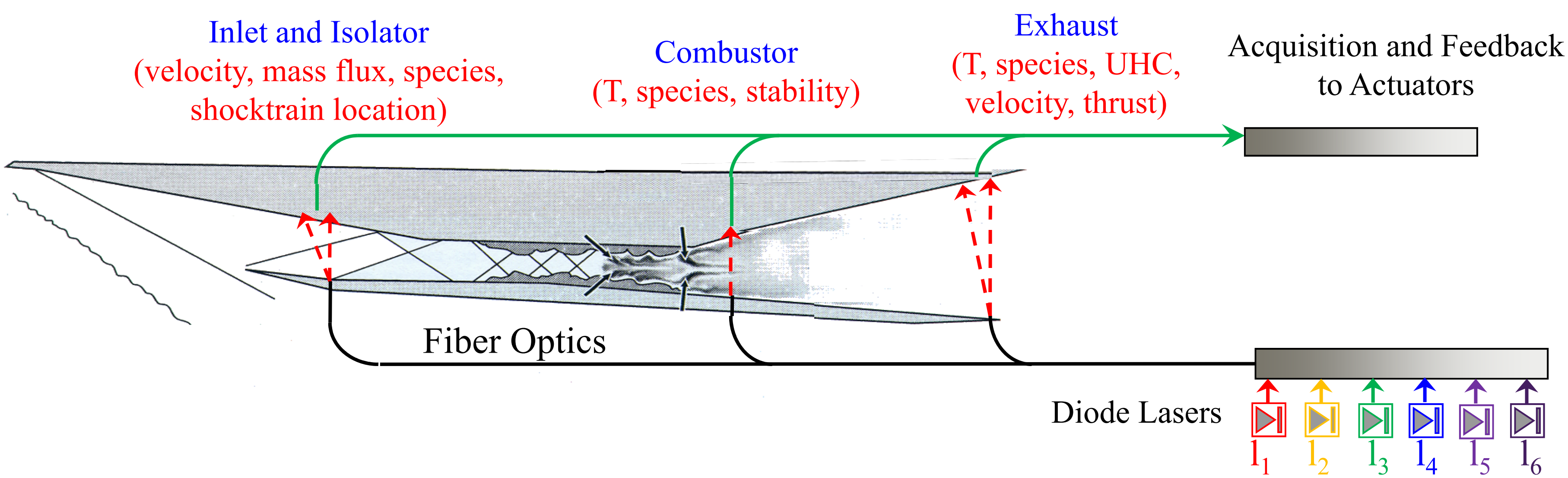
Statistical Mechanics: Defines T!

Hence measurements of two densities n_i and $n_j \rightarrow T$

Since $n_i/n_j = g_i/g_j \exp(-(\varepsilon_i-\varepsilon_j)/kT)$

4. Working Example – 1

- TDL sensing for aero-propulsion
  - Diode laser absorption sensors offer prospects for time-resolved, multi-parameter, multi-location sensing for performance testing, model validation, feedback control



- Sensors developed for T, V, H_2O, CO_2, O_2, & other species
- Prototypes tested and validated at Stanford
- Several applications successful in ground test facilities
- Now being utilized in flight

4. Working Example – 2

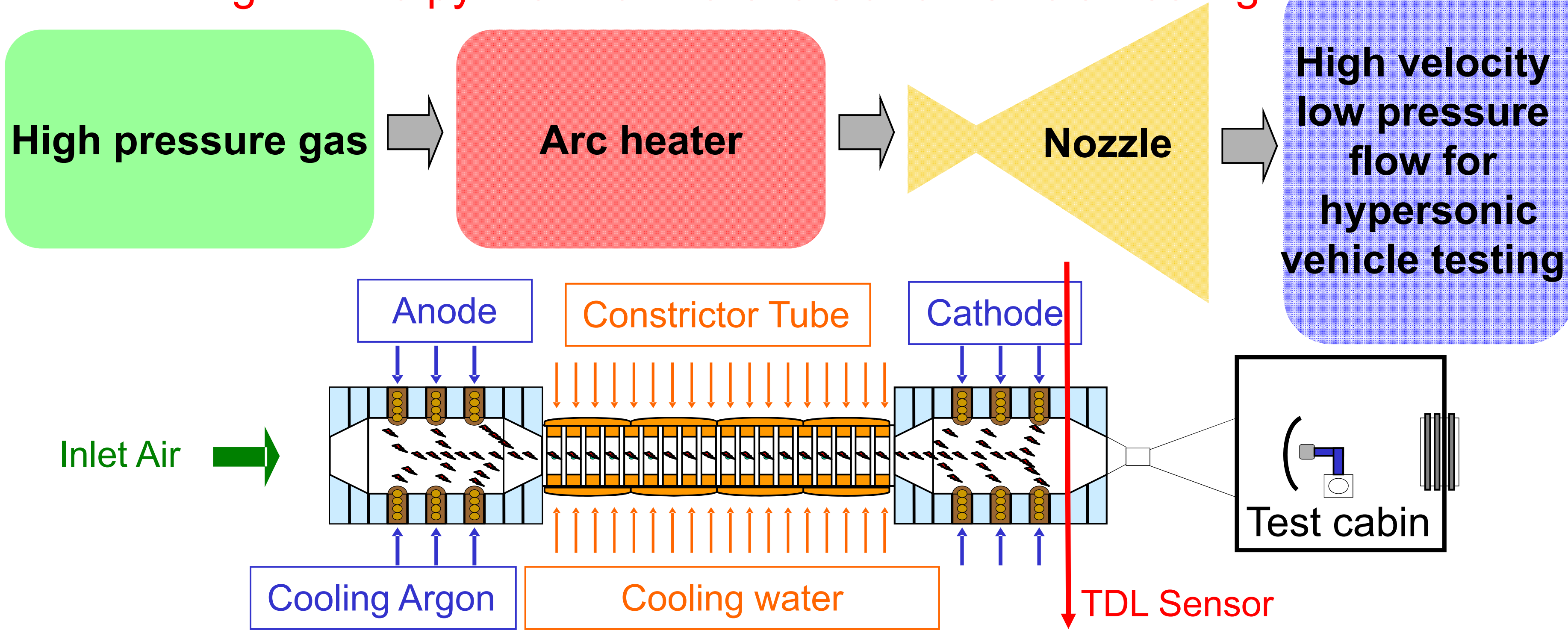
- TDL Sensing to Characterize NASA Ames ArcJet Facilities
  High-Enthalpy Flow for Materials and Vehicle Testing

High pressure gas → **Arc heater** → **Nozzle** → **High velocity low pressure flow for hypersonic vehicle testing**

4. Working Example – 2

TDL Sensing to Characterize NASA Ames ArcJet Facilities

High-Enthalpy Flow for Materials and Vehicle Testing



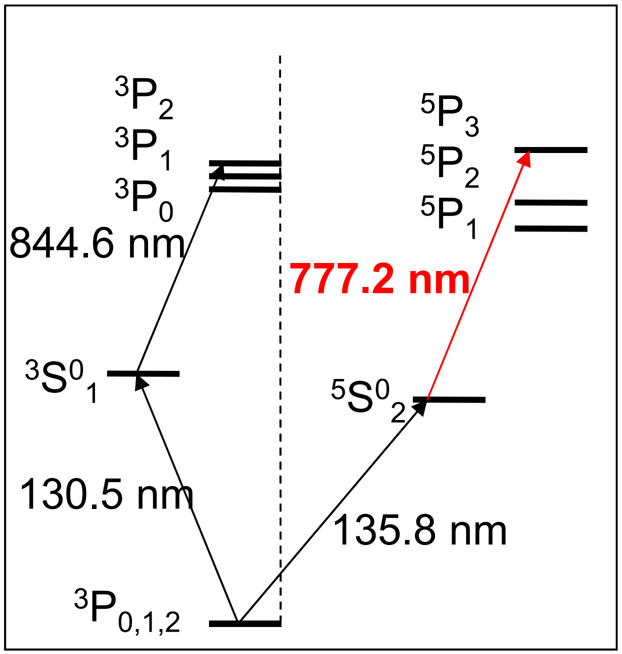
- **Goals:** (1) Time-resolved temperature sensing in the arc heater: O to infer T
  (2) Investigate spatial uniformity within heater (multi-path absorption)

Challenges: Extreme Conditions T=6000-8000K, P= 2-9 bar, I~2000A, 20 & 60 MW
Difficult access (mechanical, optical, and electrical)

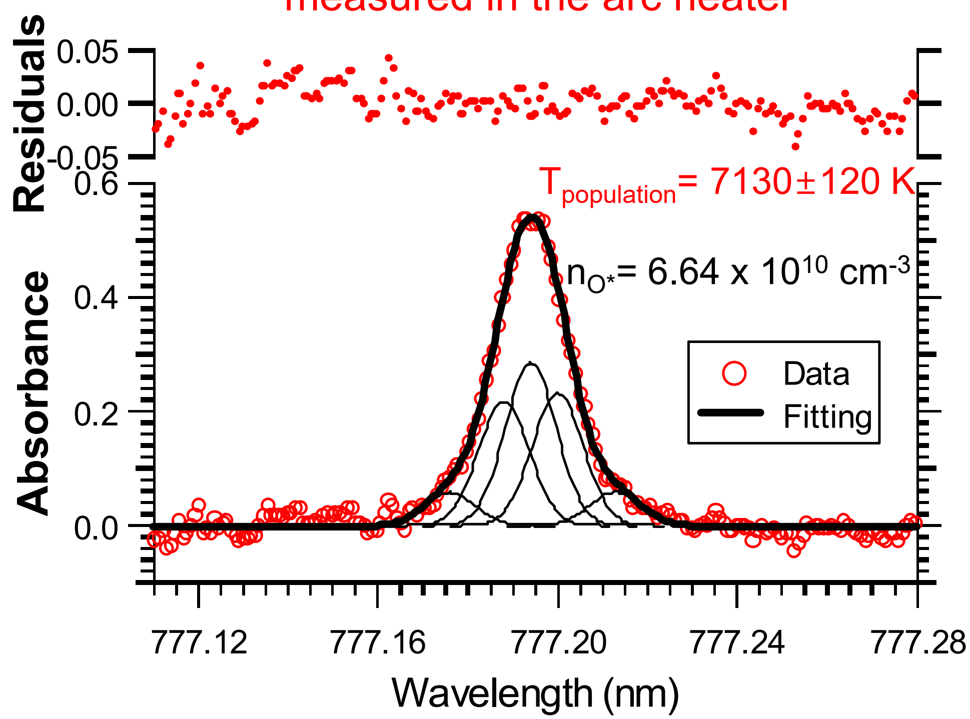
4. Working Example – 2

- Temperature from Atomic O Absorption Measurement

Atomic oxygen energy diagram



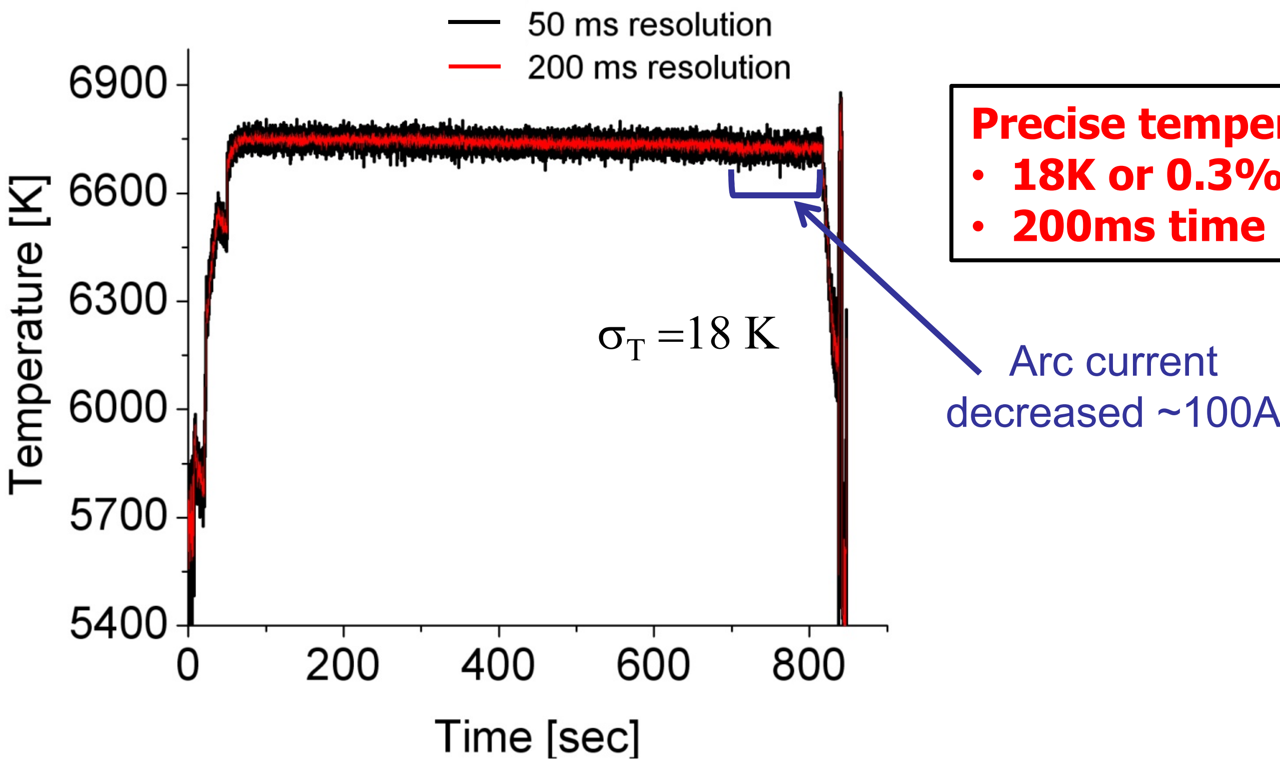
Atomic oxygen absorption measured in the arc heater



- Fundamental absorption transitions from O are VUV but excited O in NIR
- Equilibrium population of O-atom in $^5S^0_2$ extremely temperature sensitive

4. Working Example – 2

- Arc current at 2000A, power 20MW
- Last 200 seconds of run arc current decreased 100A
- Measured temperature captures change in arc conditions

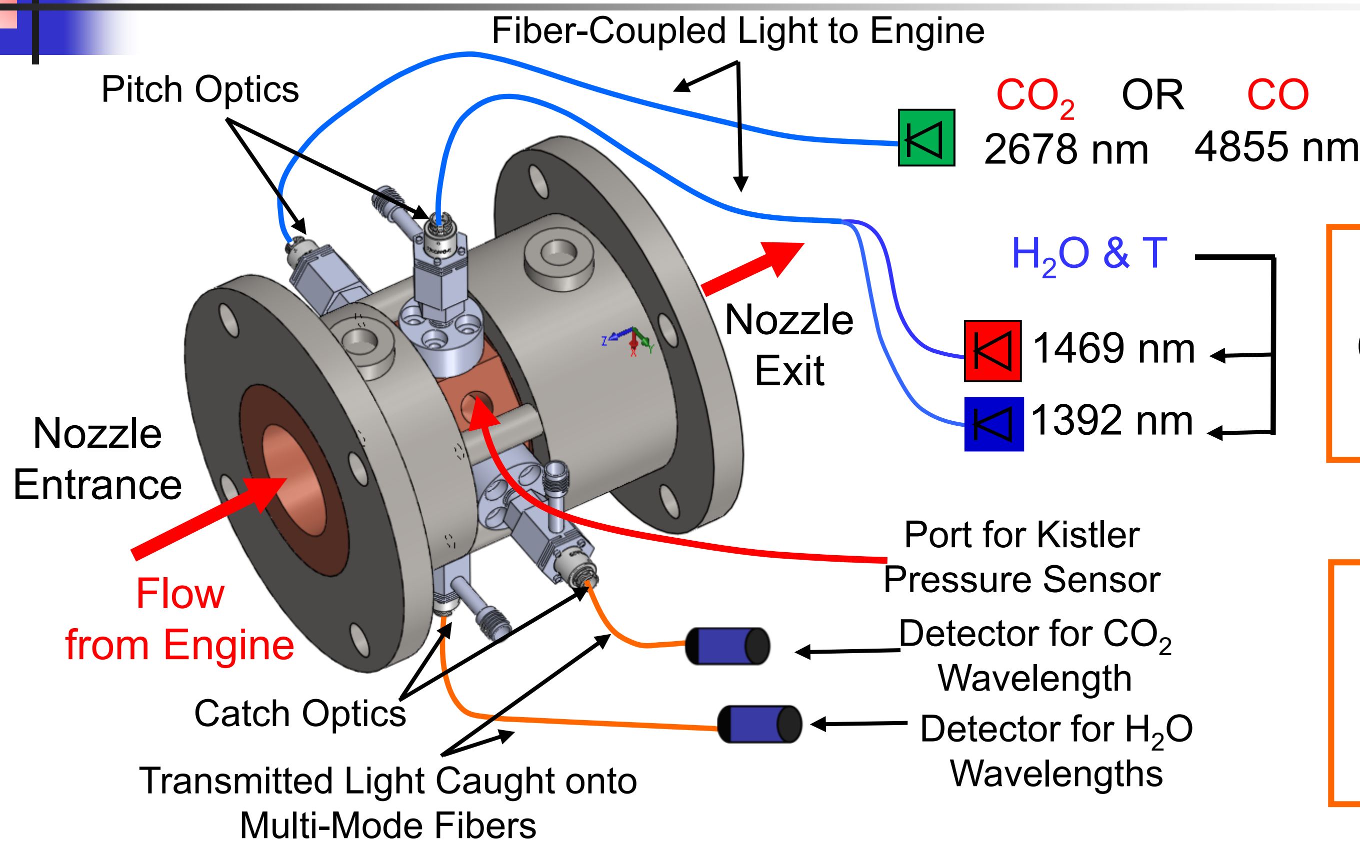


Precise temperature measurements
- **18K or 0.3% standard deviation**
- **200ms time resolution**

TDL sensor provides new tool for routine monitoring of arcjet performance

4. Working Example – 3

Time-Resolved High-P Sensing in PDC at NPS



Assumption: Choked flow T gives velocity

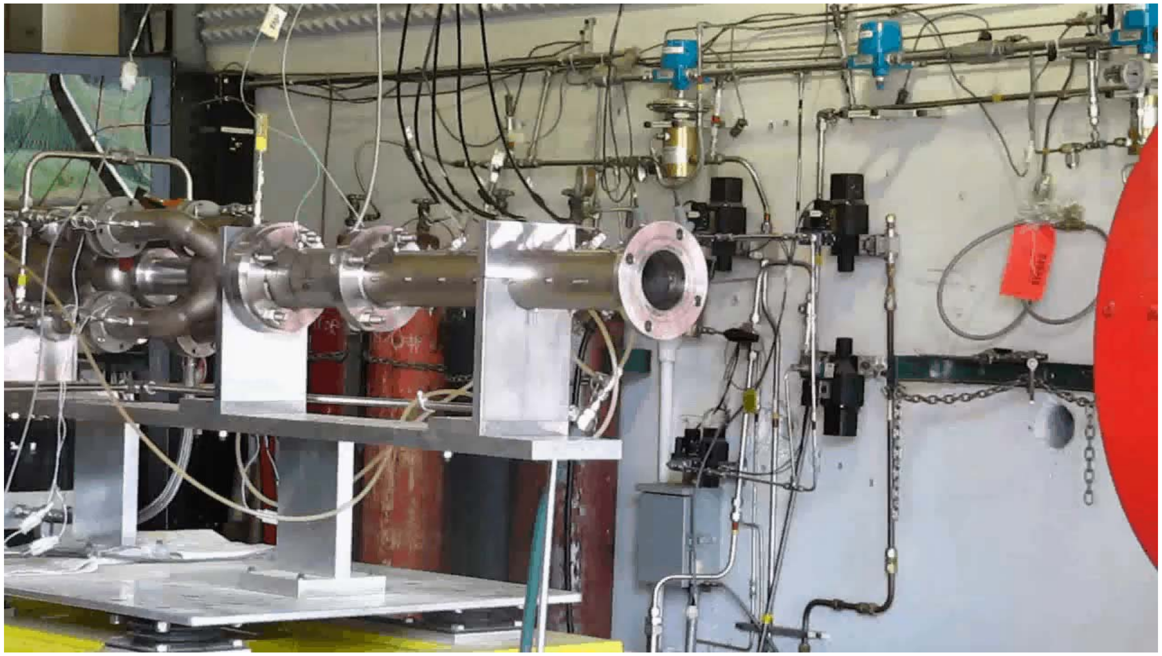
T, P, V & X_i yields Enthalpy Flux

- Pulse-detonation combustor gives time-variable P/T
- Time-resolved measurements monitor performance & test CFD

4. Working Example – 3
Time-Resolved High-P Sensing in PDC at NPS

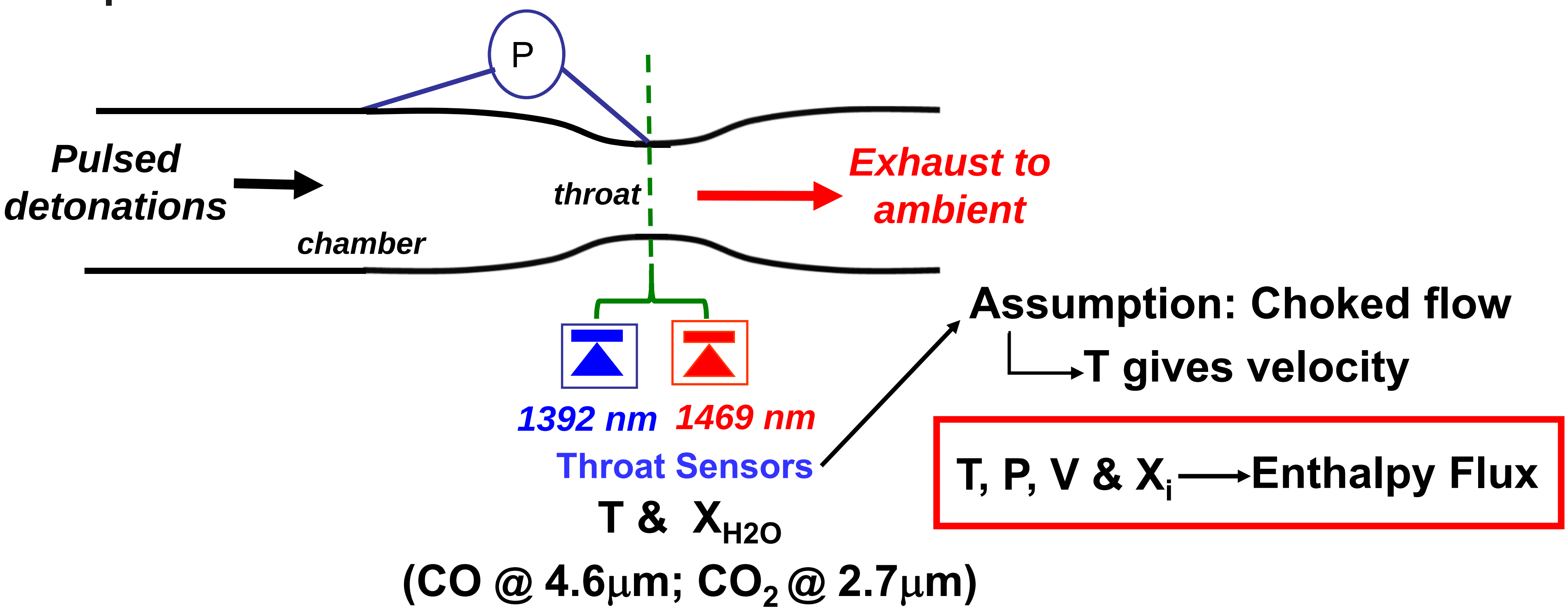
Pulse Detonation Combustor

At Naval Post-graduate School in Monterey, CA



Optical sensors feasible in harsh, high pressure engine environment

4. Working Example – 3
Time-Resolved High-P Sensing in PDC at NPS

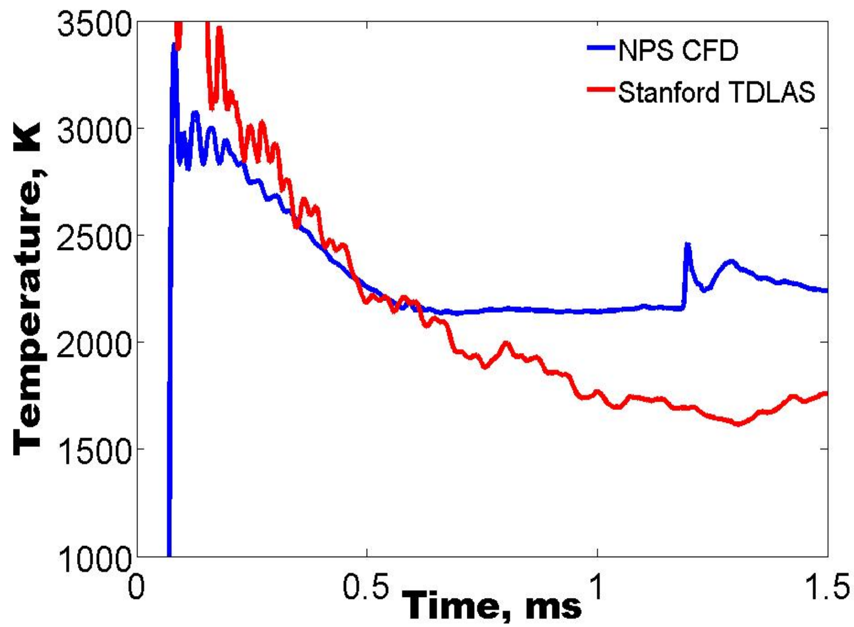


- Pulse-detonation combustor gives time-variable P/T
- Time-resolved TDLAS measurements monitor performance & test CFD

4. Working Example – 3

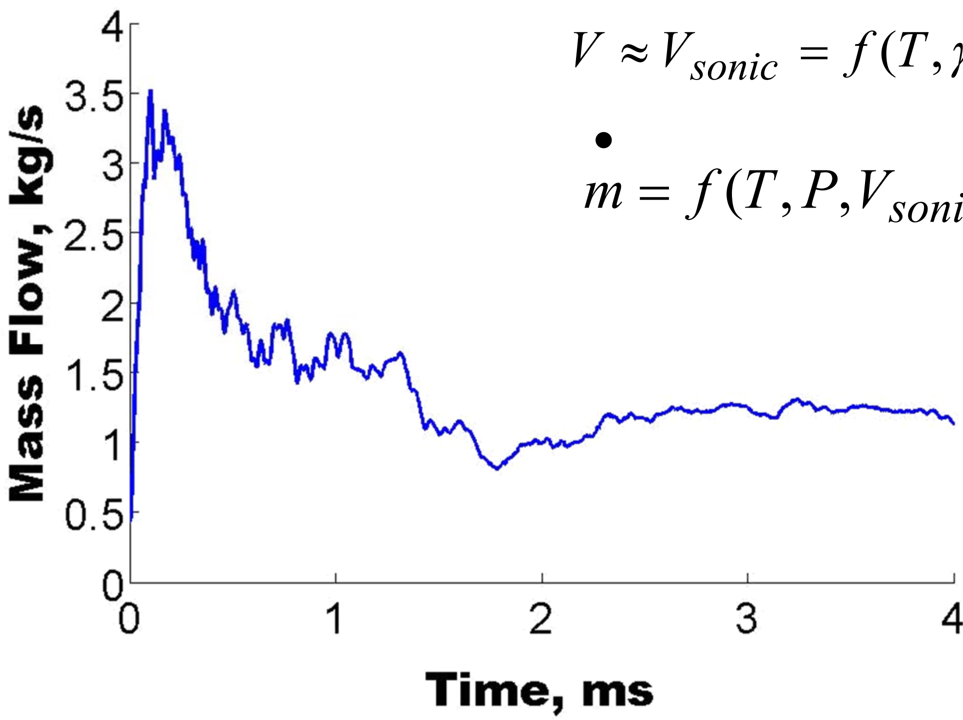
Time-Resolved High-P Sensing in PDC at NPS

T- Data Collected in Nozzle Throat vs CFD



- T sensor performs well to >3500K, 30 atm!
- Data agrees well with CFD during primary blow down

4. Working Example – 3
Time-Resolved TDLAS Yields Mass Flow



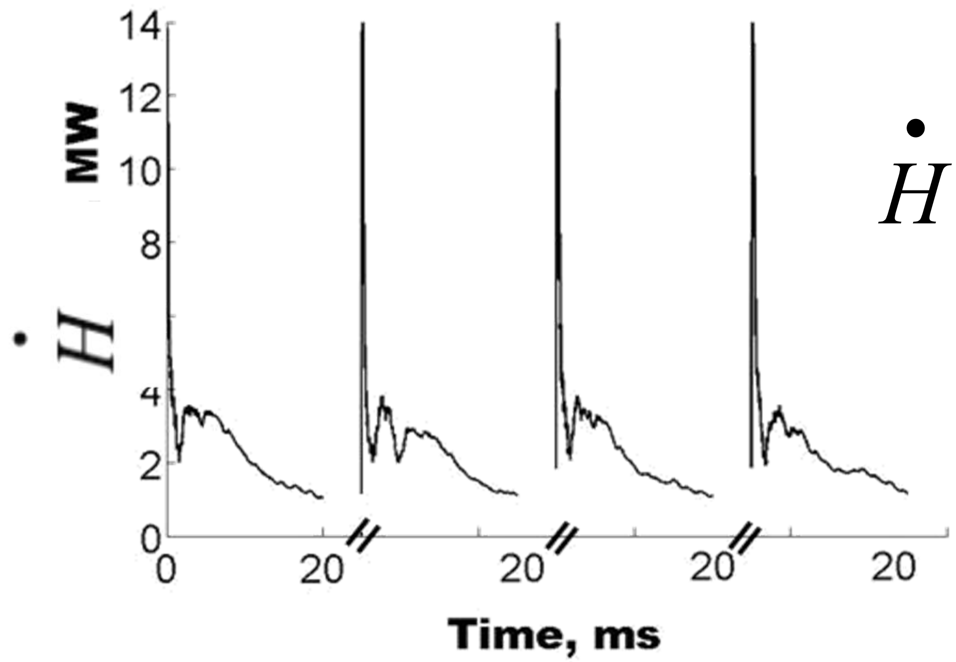
$$V \approx V_{sonic} = f(T, \gamma_{mix})$$

$$\dot{m} = f(T, P, V_{sonic})$$

- T and P give V and mass flow in choked throat as f(t)
- T, $\dot{m}$, species (CO, CO_2, H_2O) and ideal gas law can give enthalpy flow rate

4. Working Example – 3
Time-Resolved TDL Yields Enthalpy Flow Rate

4 Consecutive Cycles



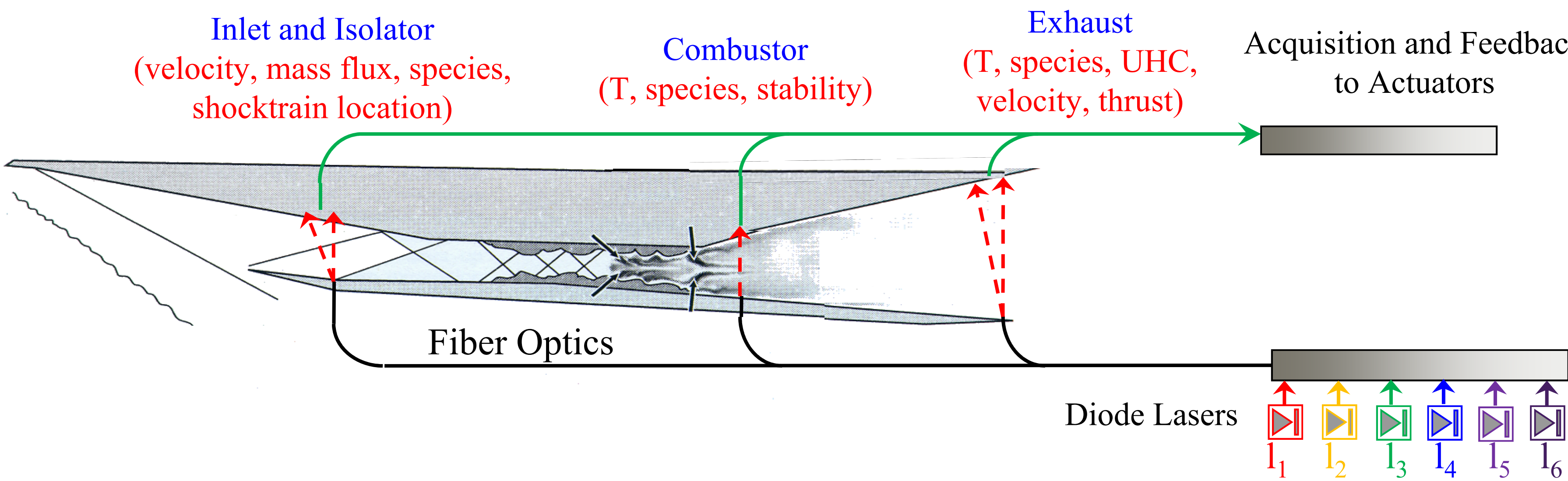
$$\dot{H} = \dot{m}\,\Delta h_{stag}(T)$$

T_{ref} = 298 K

- Time-resolved data provide key measures of engine performance
  - Power (enthalpy flux)
  - Mass flow dynamics
  - H integrated over complete cycle for η_{th}

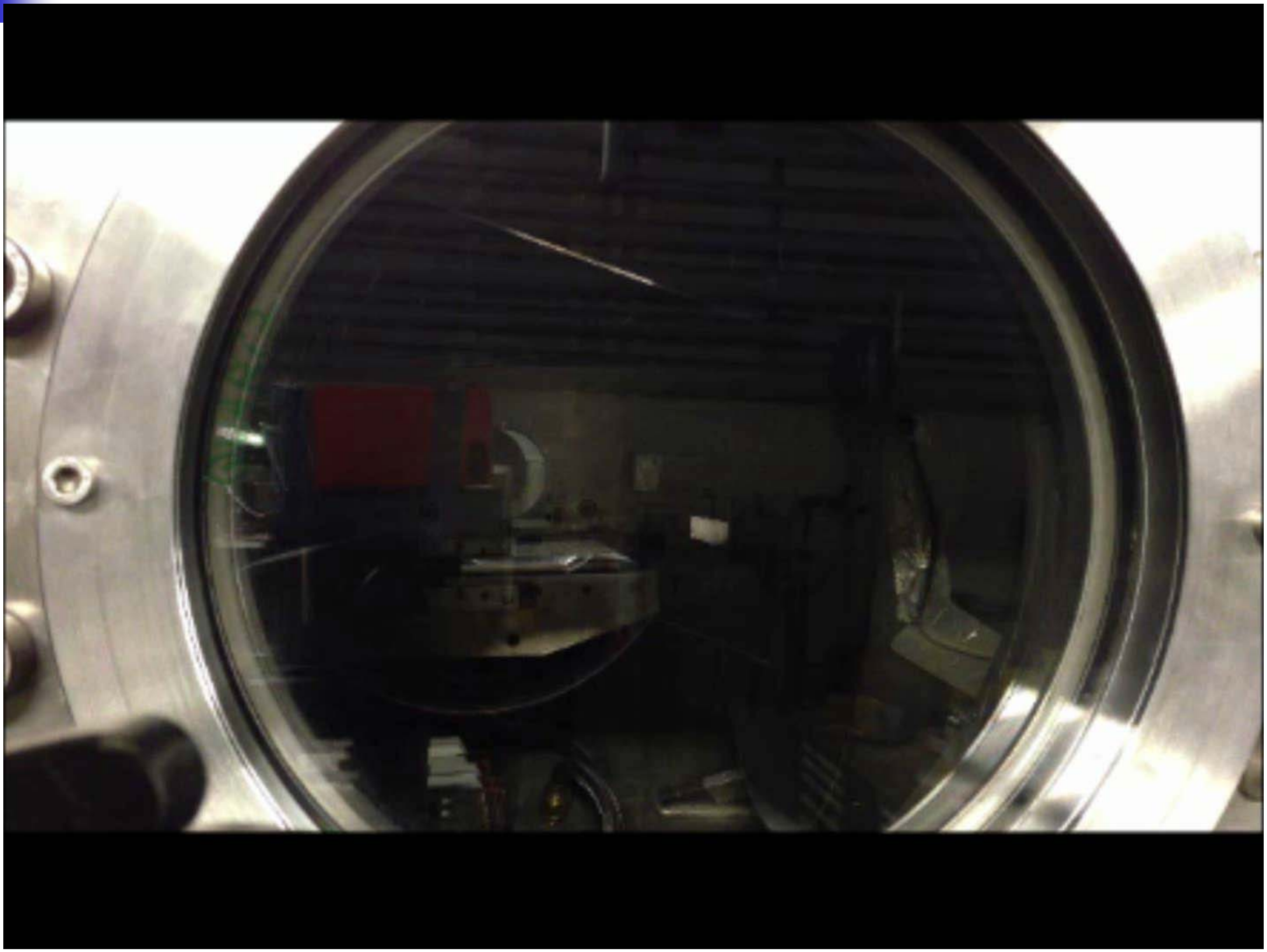
4. Working Example – 4
Time-Resolved Sensing in HEG Shock Tunnel

– Diode laser absorption sensors offer prospects for time-resolved, multi-parameter, multi-location sensing for performance testing, model validation, feedback control

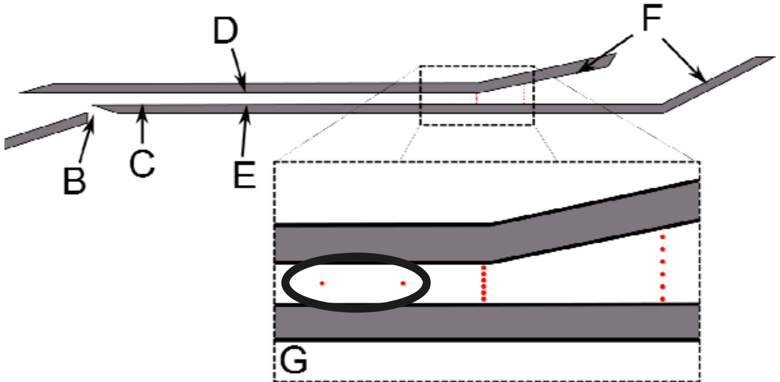


- Sensors developed for T, V, H_2O, CO_2, O_2, & other species
- Prototypes tested and validated at Stanford
- Several successful demonstrations in ground test facilities
- Opportunities emerging for use in flight: **sensing and control**
- Measurements made in Mach 7.4 shock tunnel in Germany

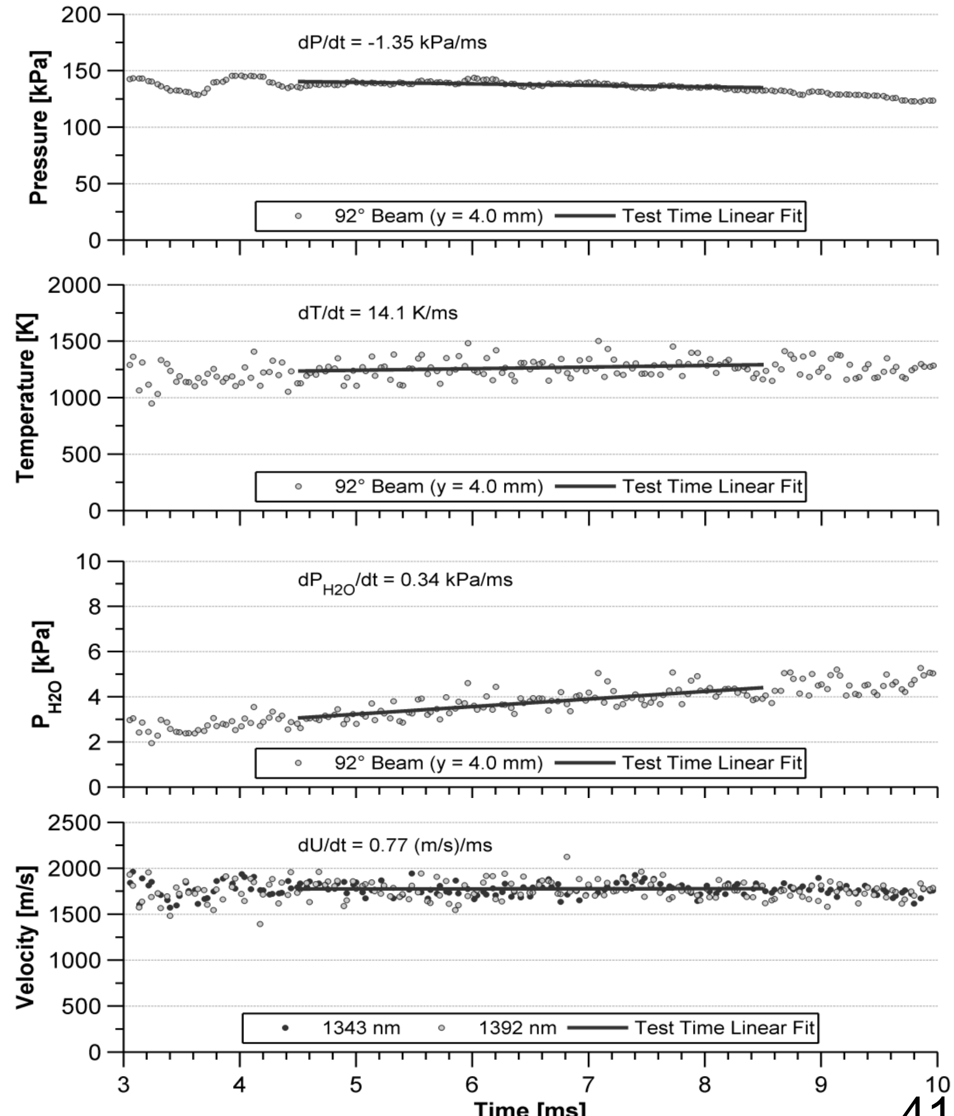
4. Working Example – 4
Time-Resolved Sensing in HEG Shock Tunnel



4. Working Example – 4
Time-Resolved Sensing in HEG Shock Tunnel

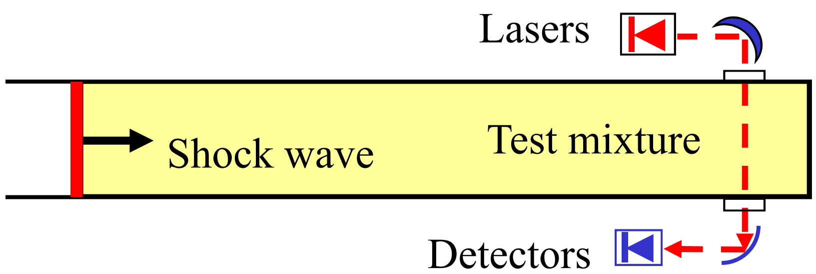


		$\bar{x} \pm \sigma$	dx/dt [1/ms]
P	[kPa]	137.7 ± 2.5	-1.35
P_{H_2O}	[kPa]	3.7 ± 0.5	0.34
T	[K]	1264 ± 81	14.1
U	[m/s]	1776 ± 82	0.77



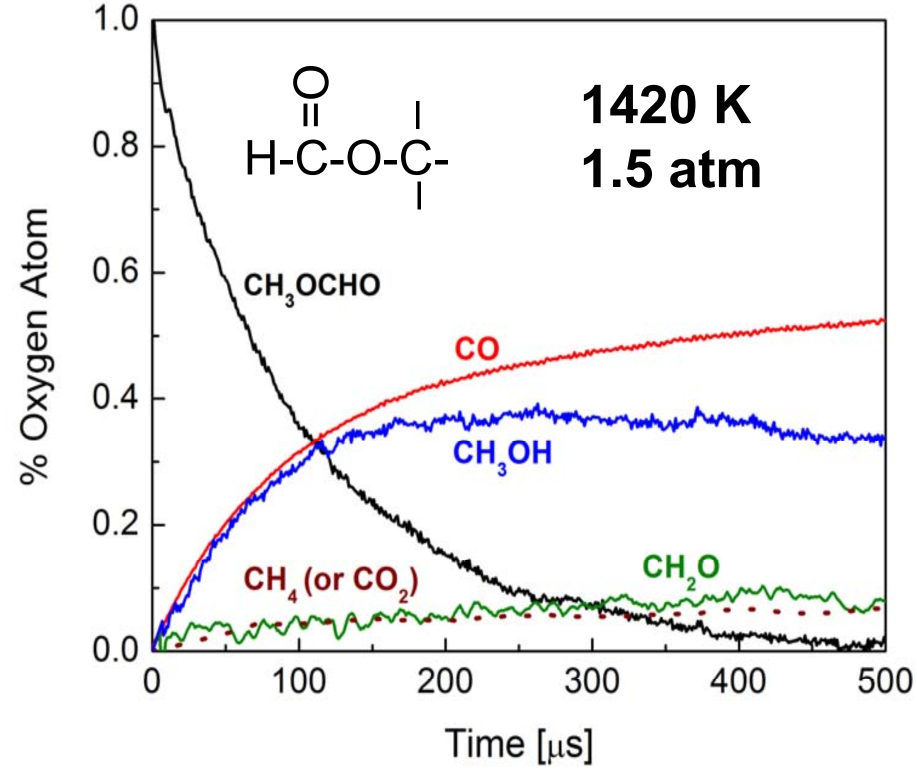
4. Working Example – 5

First Multi-Species Sensing for Shock Tube Kinetics



- Chemistry progress monitored by quantitative IR laser absorption
- Multi-species time histories provide game-changing advantage for mechanism validation
- Method accounts for nearly 100% of O-atoms

Oxygen Balance: Methyl Formate Decomposition



Next: Diatomic Molecular Spectra

- Rotational and Vibrational Spectra