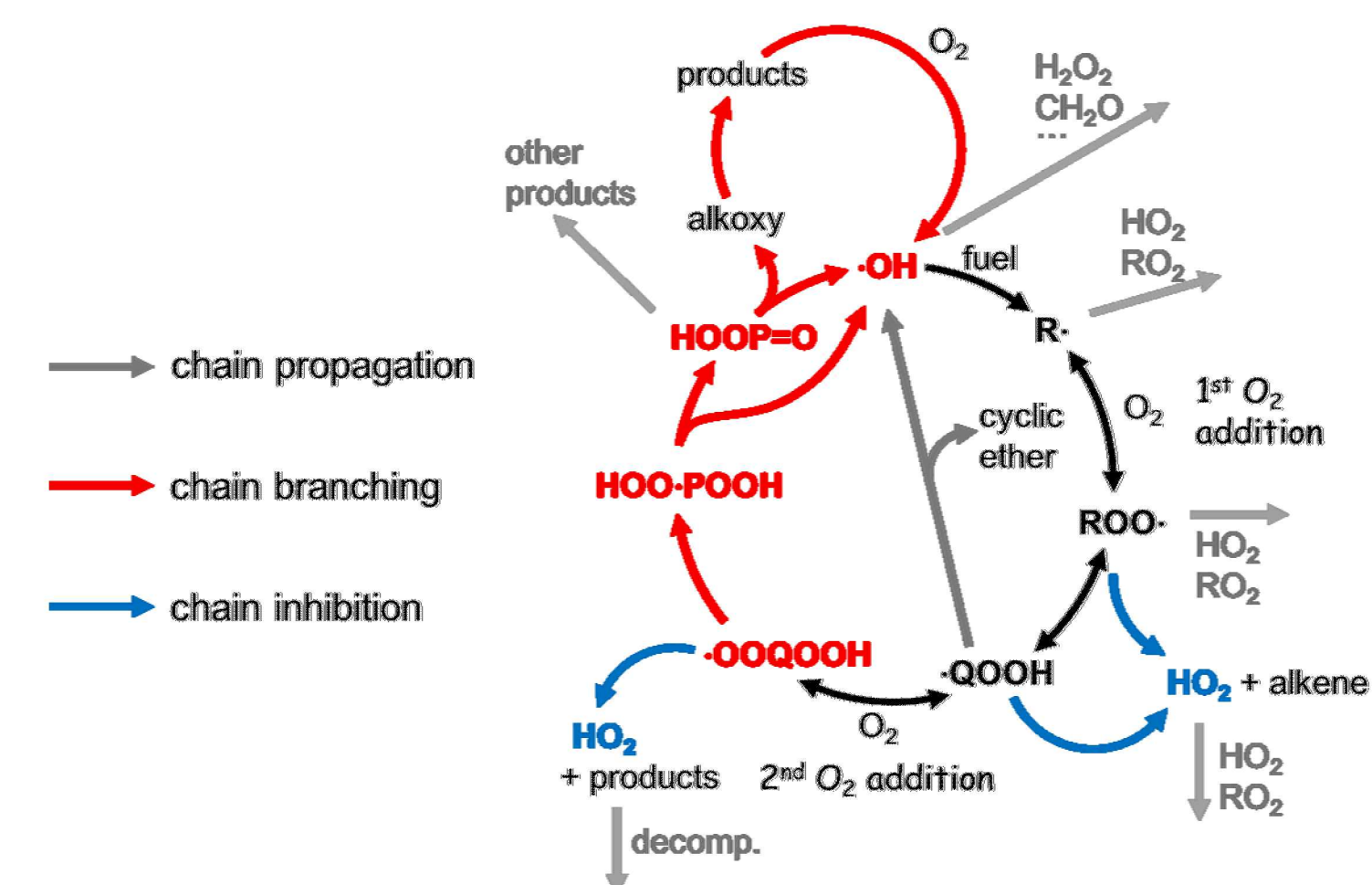


Coupling FAGE Detection of OH and HO₂ with a High-Pressure Reactor for Biofuel Characterization

Zachary Buras, Kendrew Au, Cosmin Safta, Judit Zádor, Leonid Sheps
Combustion Research Facility, Sandia National Laboratories, Livermore, CA

I. Motivation

OH and HO₂ Radicals are the main drivers of low-temperature fuel autoignition:¹

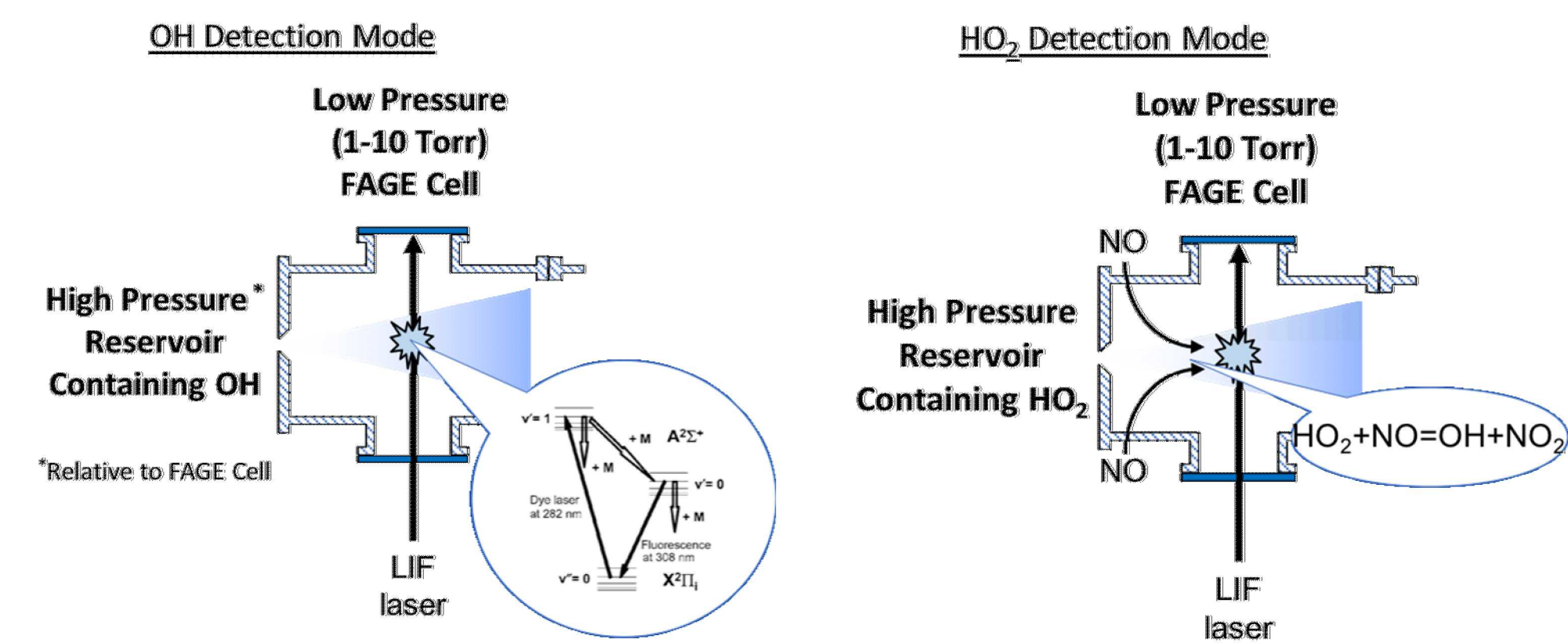


However, both radicals are difficult to detect at engine-relevant conditions (high pressure) using common techniques:

- Mass Spectrometry → High ionization potentials and low cross sections²
- Laser Absorbance → Broadening of spectral features
- Fluorescence → Significant quenching

II. Introduction to FAGE*

*Fluorescence Assay by Gas Expansion



Rather than directly perform Laser Induced Fluorescence (LIF), gas is first sampled into a low pressure cell, which has two benefits:

- Lower [M] reduces quenching rate
- FAGE can be operated in "HO₂ Detection Mode" by mixing in NO with sampled gas

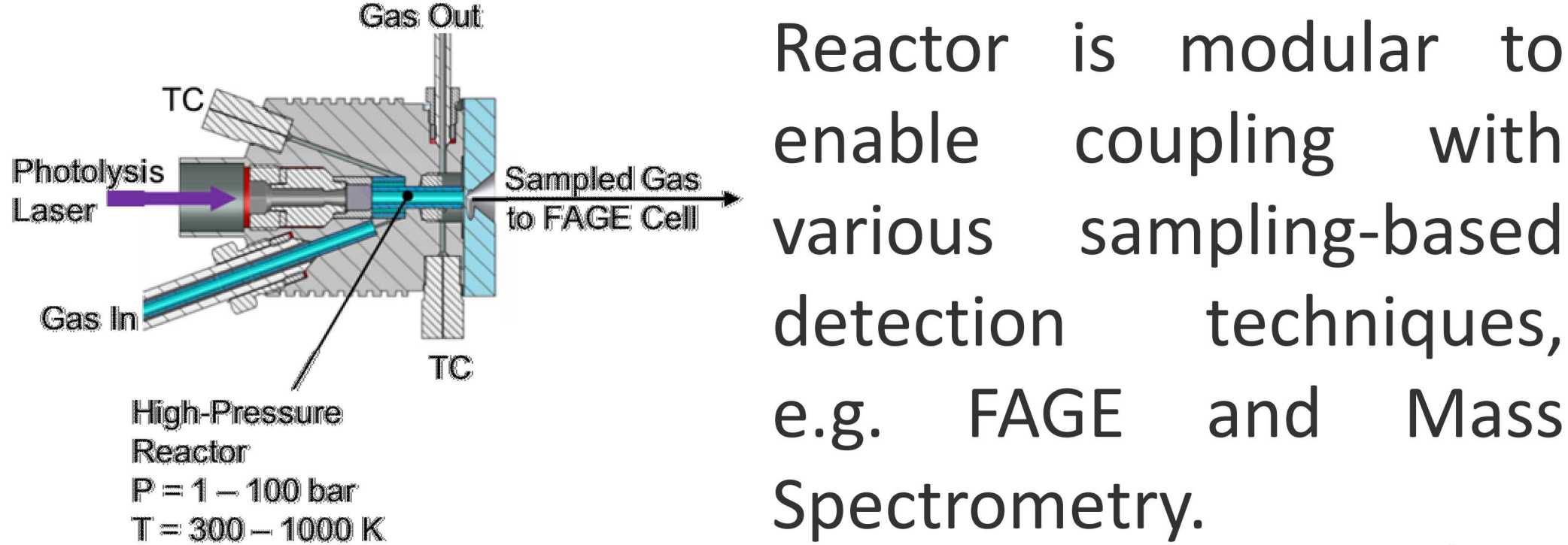
However, sampling process reduces [OH]/[HO₂] and introduces a transport delay. Obtaining sensitive, time-resolved [OH]/[HO₂] from FAGE therefore requires careful design.

III. Design of Apparatus

Apparatus consists of two parts:

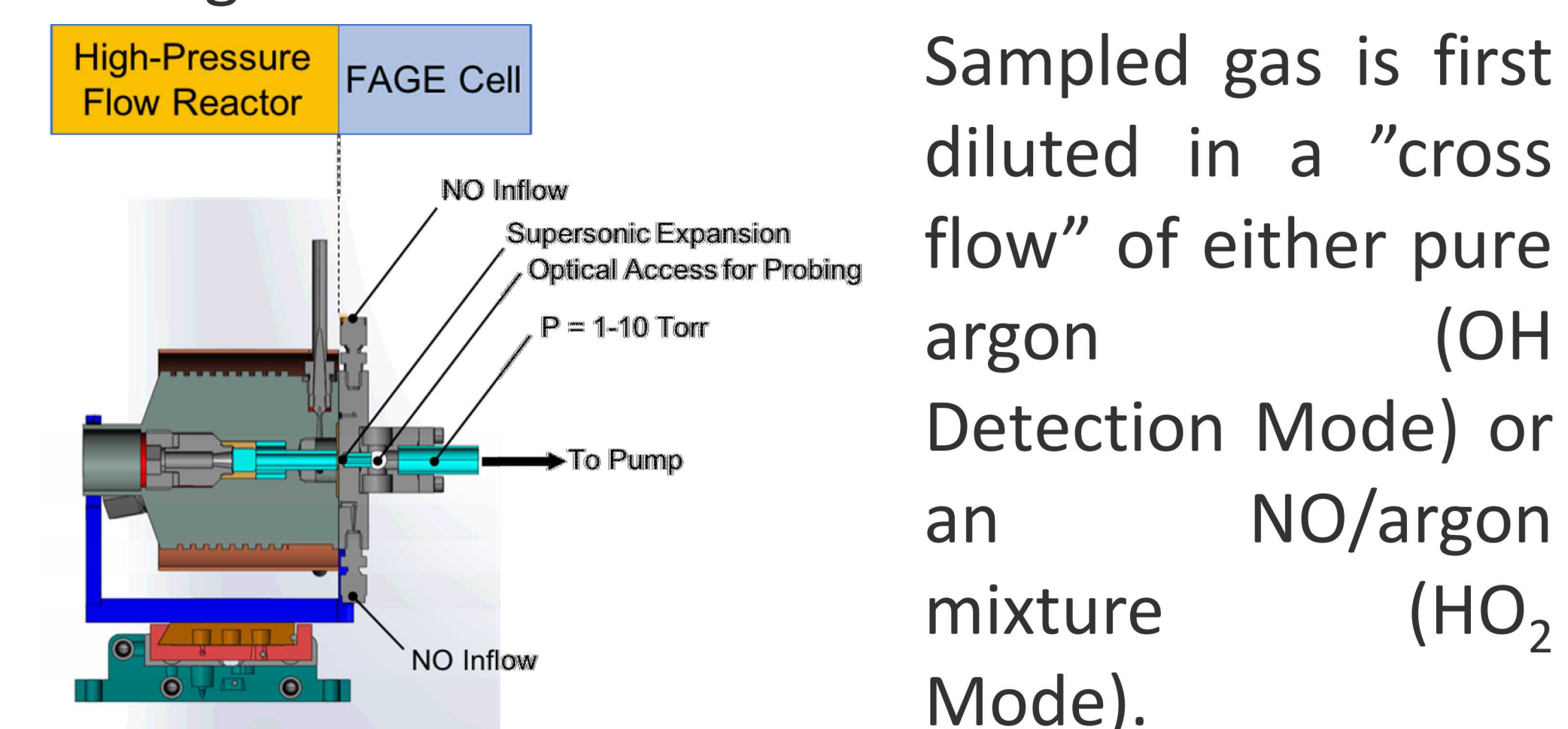
- High-pressure reactor
- Low-pressure FAGE cell

Reactor is a quartz flash-photolysis cell inside of a heated stainless steel block:

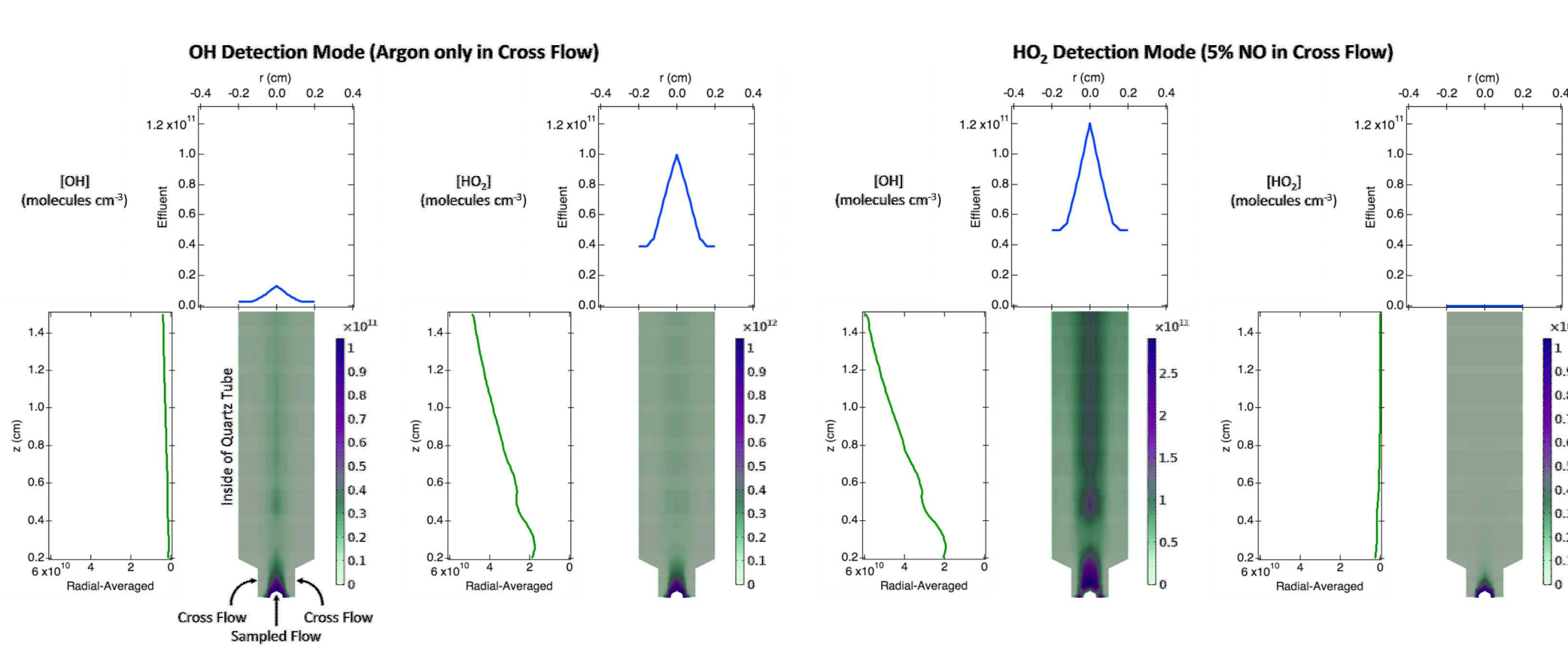


Reactor is modular to enable coupling with various sampling-based detection techniques, e.g. FAGE and Mass Spectrometry.

A wide range of gas residence times are accessible, which is necessary when flowing flammable mixtures at elevated temperatures:

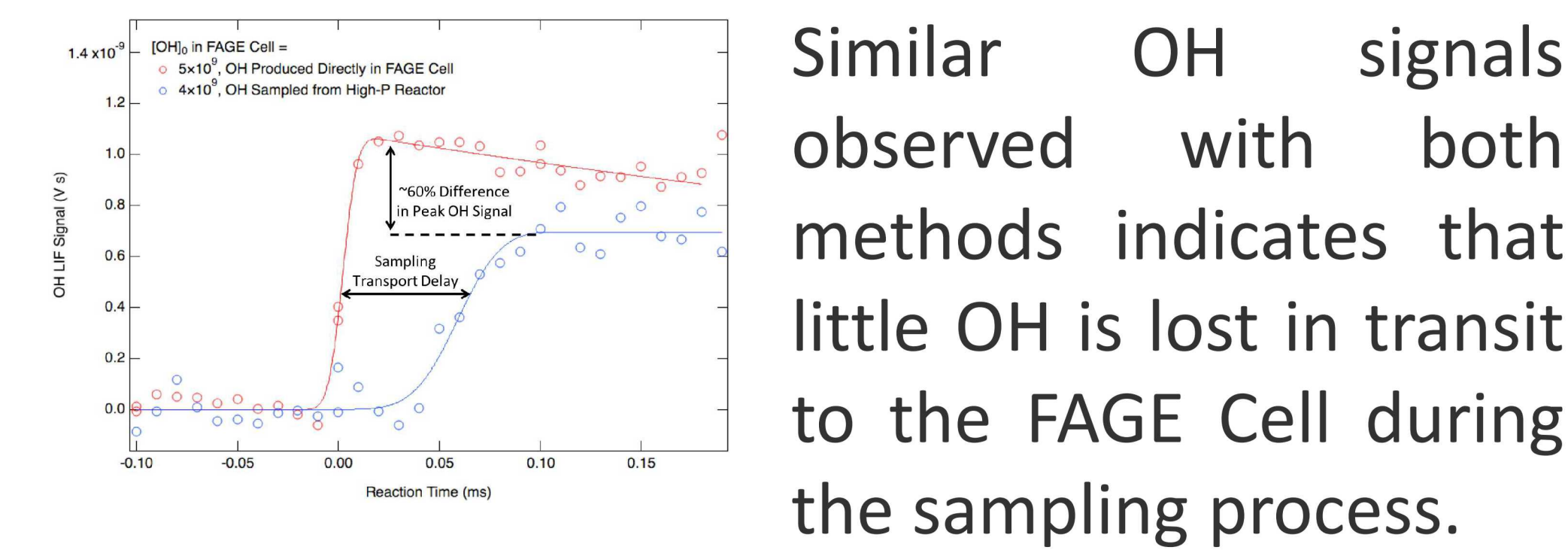


FAGE Cell is a low pressure chamber with optical access in two dimensions for LIF laser and orthogonal fluorescence detection:



IV. Testing of Apparatus

Similar concentrations of OH were generated in the FAGE cell in 10 Torr argon via two methods:



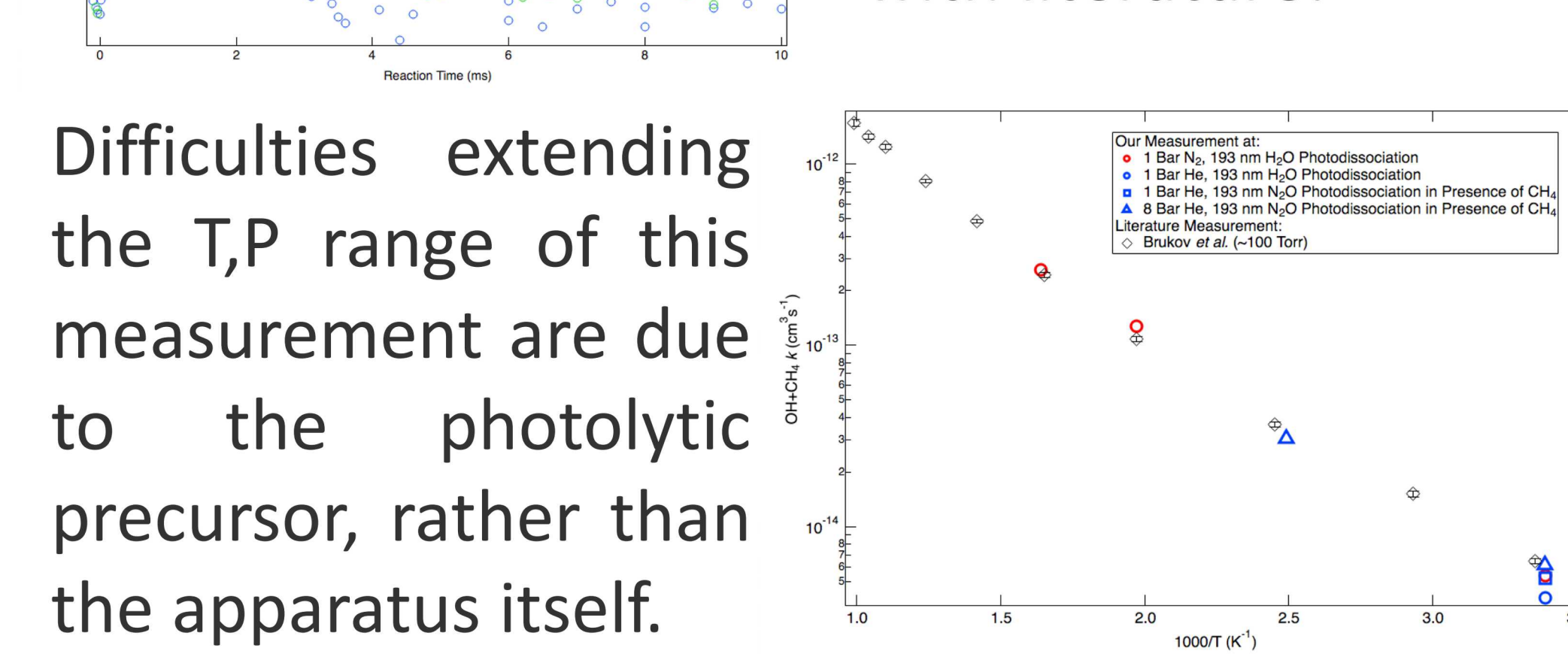
Similar OH signals observed with both methods indicates that little OH is lost in transit to the FAGE Cell during the sampling process.

Similar [OH] produced via different photolytic routes also yields similar signals, indicating the reproducibility of FAGE detection:

Measured detection limit is ~1x10⁸ molecules cm⁻³ of OH in the FAGE Cell. Accounting for a three orders of magnitude reduction in [OH] during the sampling process, the detection limit in the high-pressure reactor is therefore ~1x10¹¹ molecules cm⁻³.

Measured time resolution at chosen operating conditions is ~50 μs, close to the expected value of 100 μs:

Both the sensitivity and time resolution of the apparatus are sufficient to measure OH kinetics over a range of conditions:



Difficulties extending the T,P range of this measurement are due to the photolytic precursor, rather than the apparatus itself.

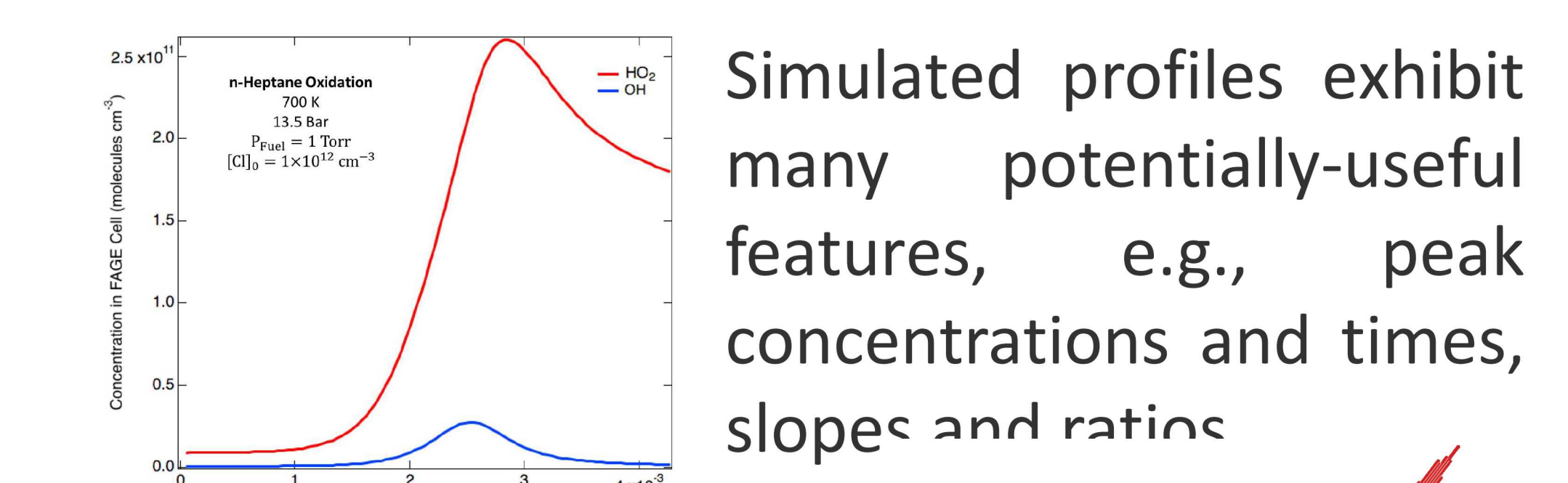
V. Future Work

Two critical experiment tests remain:

- Measure HO₂ with FAGE, using photolytically-initiated methanol oxidation as the HO₂ source.
- Extend T,P range over which both OH and HO₂ have been measured with FAGE. In particular, higher pressures of N₂ bath gas need to be tested, necessitating a suitable photolytic precursor.

VI. Expected Results

Once the remaining tests above are completed, this apparatus will be used to measure time-resolved [OH]/[HO₂] during photolytically-initiated fuel oxidation. Realistic simulations that include a FAGE detection limit of 1x10⁸ molecules cm⁻³ and time resolution of 100 μs predict that profiles such as the following can be measured:



Simulated profiles exhibit many potentially-useful features, e.g., peak concentrations and times, slopes and ratios

Machine-learning tools (e.g., feed-forward neural nets) show that these features can be correlated with fuel ignition properties such as ignition delay time (IDT):

