SAND2008-2096C

Development of a Fieldable Real-Time Mercuric Chloride Monitor using Laser Photofragment Emission

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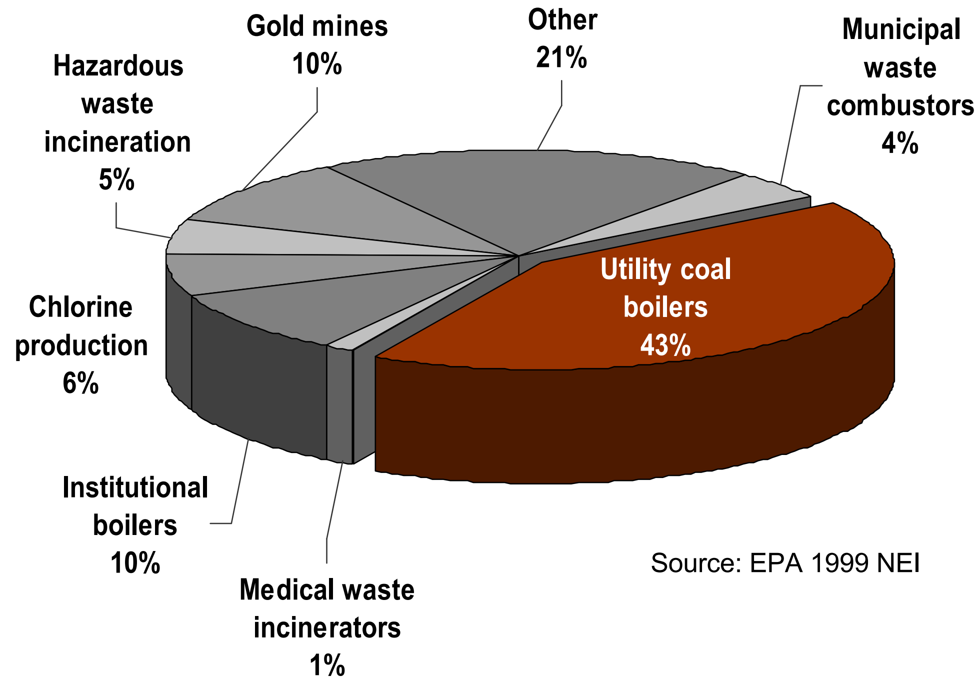
Presented at the National Meeting of the American Chemical Society, New Orleans, LA, Apr. 6th, 2008

Work sponsored by the DOE Office of Fossil Energy’s National Energy Technology Laboratory Advance Research Program (Award FEW03-011948)

The Mercury Problem

- Nation's largest source of anthropogenic mercury emissions: coal-fired power plants
- EPA's Clean Air Mercury Rule: Reduce mercury emissions by ~70% by 2018
- Gas-phase Hg exists in two forms:
  - (1) Elemental Hg (Hg^0): removed with activated carbon sorbent ($$$)
  - (2) Oxidized Hg (primarily $HgCl_2$): water soluble, removed by wet scrubbers

U.S. Hg emissions (anthropogenic)



Source: EPA 1999 NEI

Need: Quantitative, sensitive, rapid detection approach that can speciate mercury

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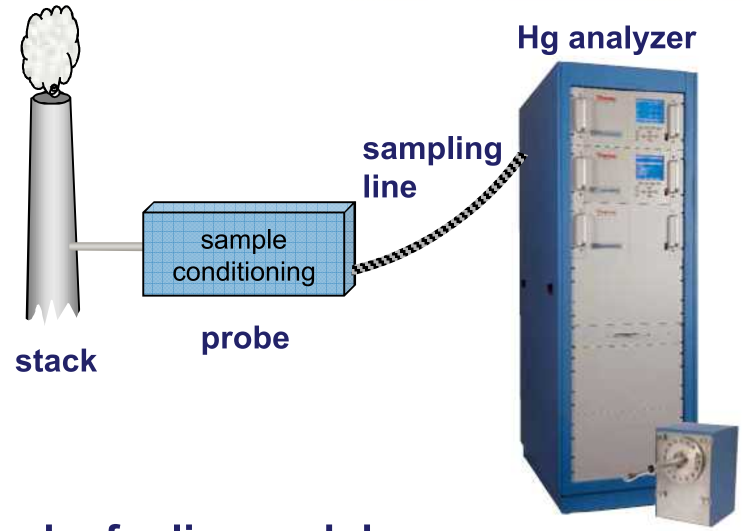
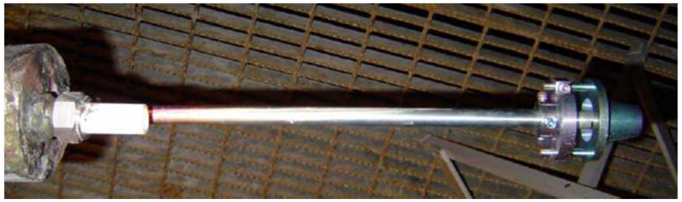
Current Mercury Detection Instruments

- Sample probe removes gas from stack
- Sample conditioning:
  - Remove Hg^{2+}, measure Hg^0
  - Reduce Hg^{2+}, measure total Hg
- Mercury analyzer
  - Atomic fluorescence/absorption using Hg-lamp optical source
  - Concentrating step
- Multiple problems associated with probe and sampling lines
  - Plugging of the probe
  - Chemical reactions within sampling lines



Probe fouling and decay


before


after

Source: R. McRanie, "Thermo Supergroup II," 2006

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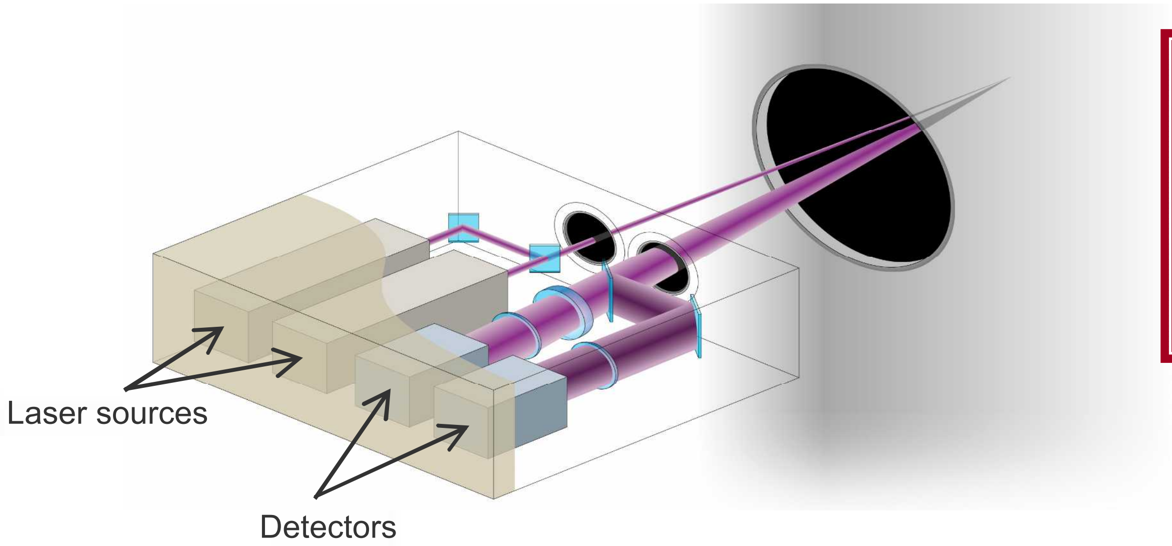
Goal: Short-range lidar approach

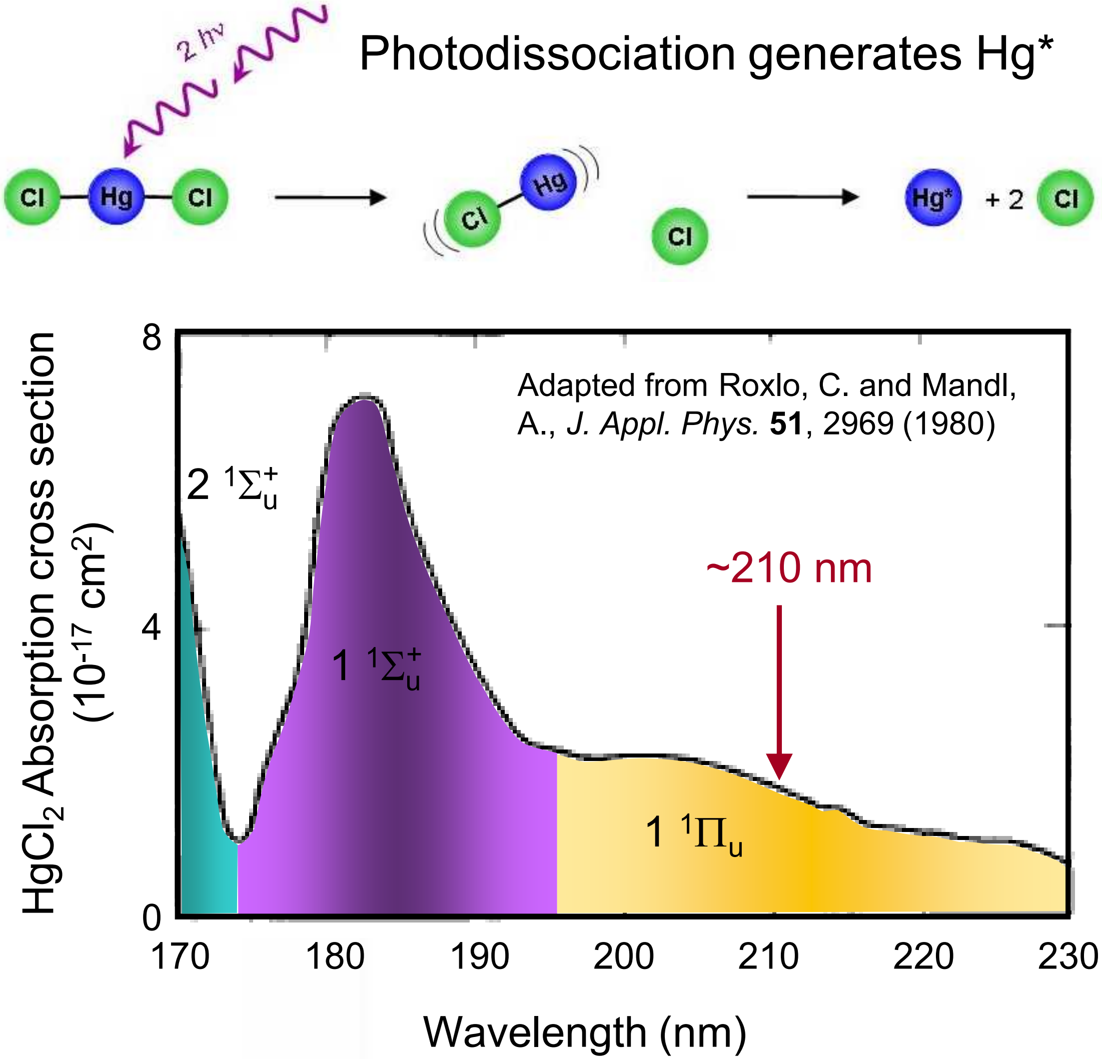
- Nominal response time of a few minutes
- Avoids issues with sampling lines and filters
- Direct extension to probing other locations or species in process stream
- Speciating mercury emissions monitor:
  - Hg^0: resonance laser-induced fluorescence (LIF) measurements
  - $HgCl_2$: detection of photofragment emission (PFE)



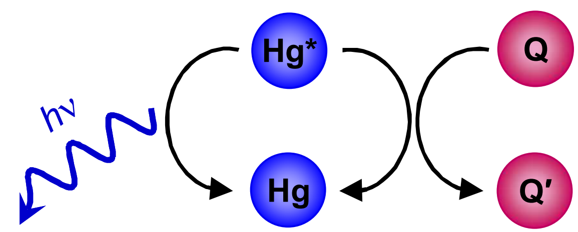
Requirements:
- Detection limit: 0.1 ppb
- Acquisition time scale: ~5 minutes

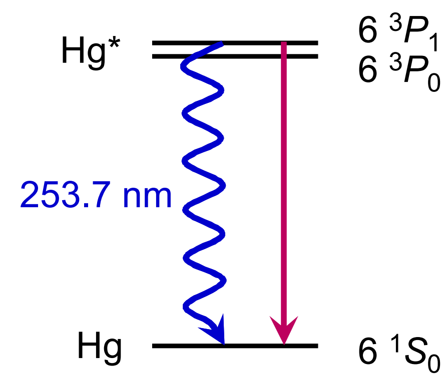
Photofragment Emission (PFE) Detection of $HgCl_2$

Photodissociation generates Hg*



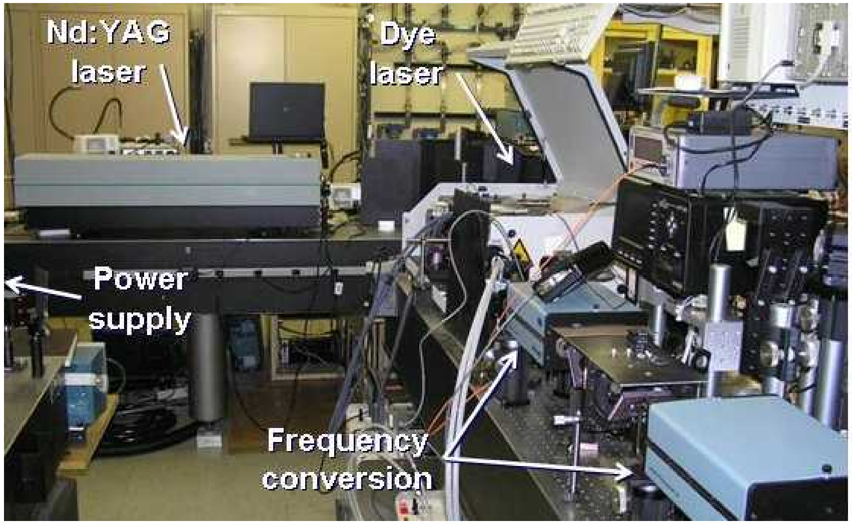
Hg* emits a photon or is collisionally quenched.



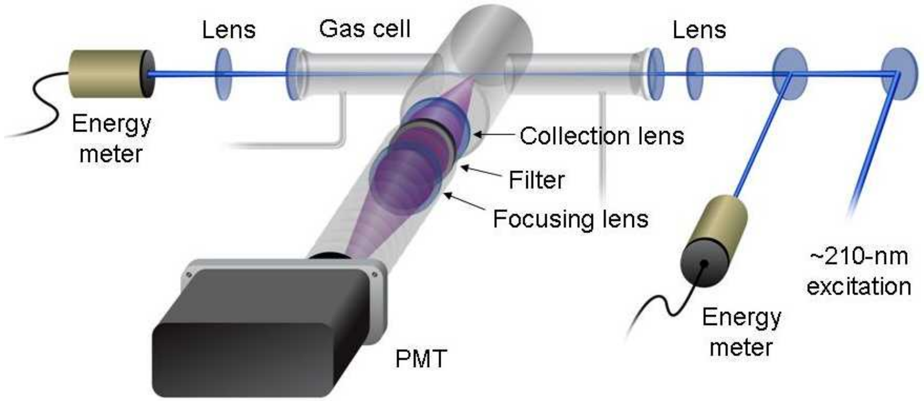


Feasibility Studies

Laboratory Laser



Test Cell and Collection Optics



- Laser tuned from 207-215 nm
- Varied pulse energy and test cell buffer gas pressure/ composition

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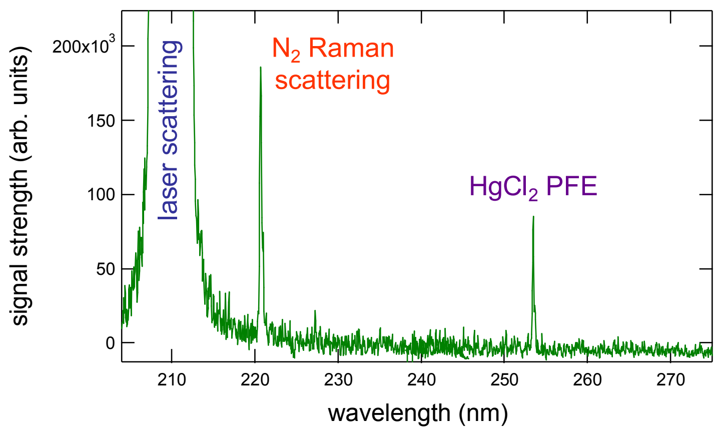
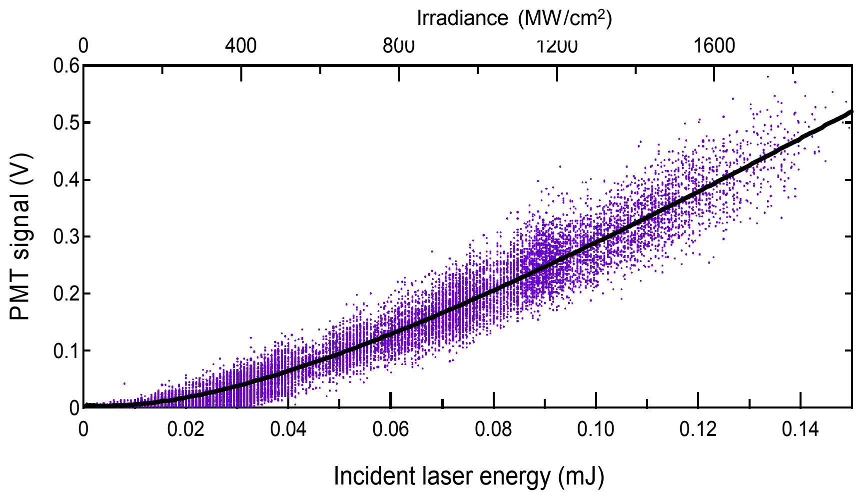
Quantifying $HgCl_2$ PFE

$HgCl_2$ PFE cross section:

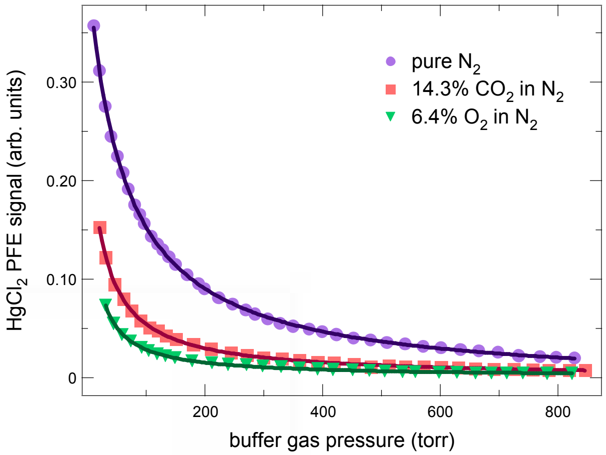
$$\sigma_{\text{PFE, 760 torr } N_2} = 1.0 \times 10^{-25}\,\text{m}^2$$



Laser irradiance dependence:



Collisional quenching:



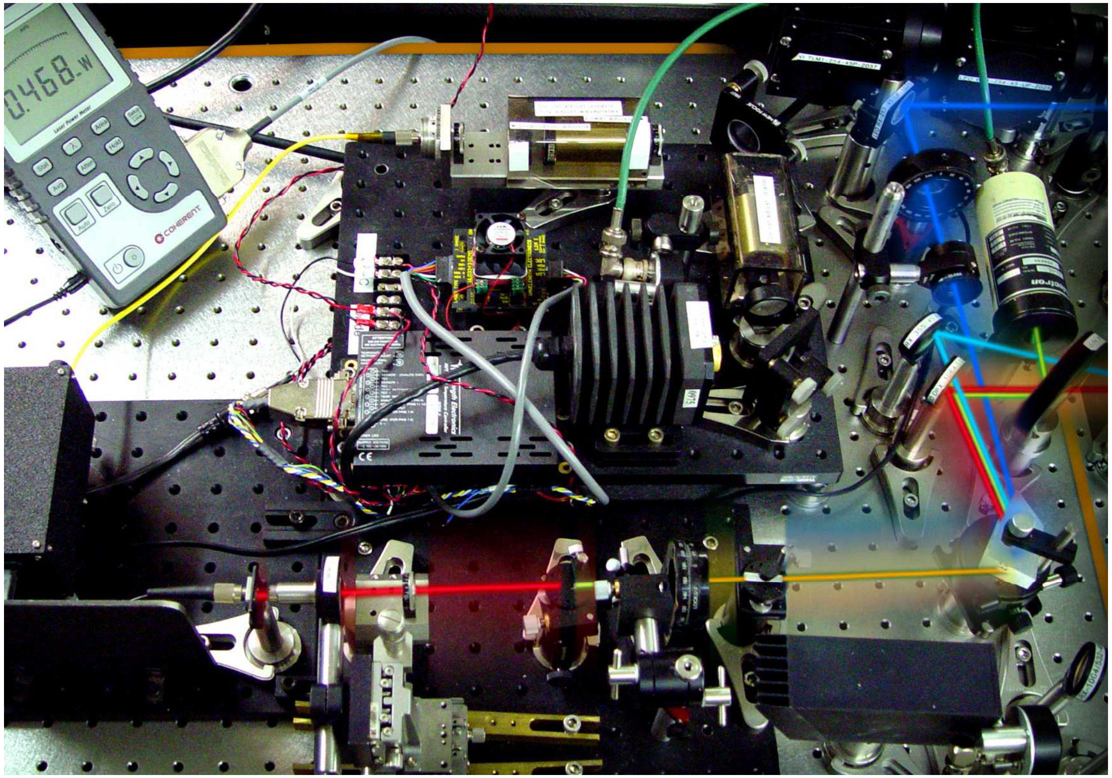
Quenching rate coefficients:

N_2: 4.20 (±0.49) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}

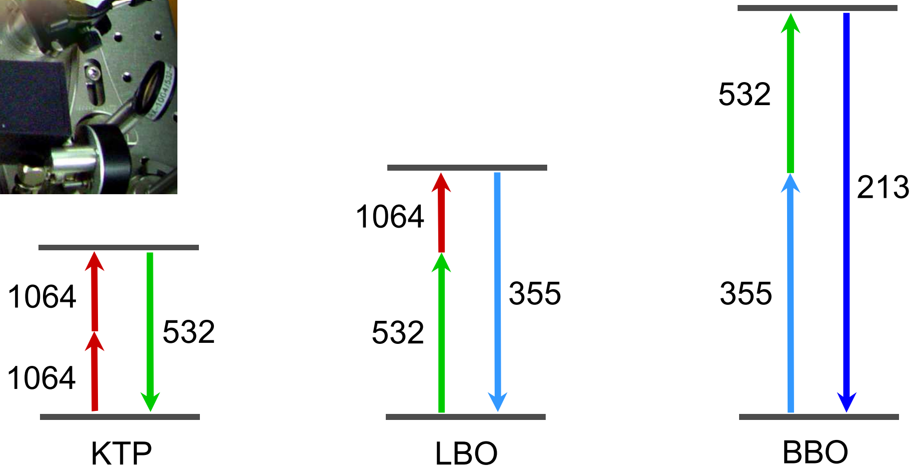
O_2: 2.87 (±0.08) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}

CO_2: 4.57 (±0.89) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}

Compact 213-nm Laser Source



- Near-IR to deep-UV conversion in single pass
- Compact, rugged, no cavities required
- 3 crystals: KTP, LBO, and BBO



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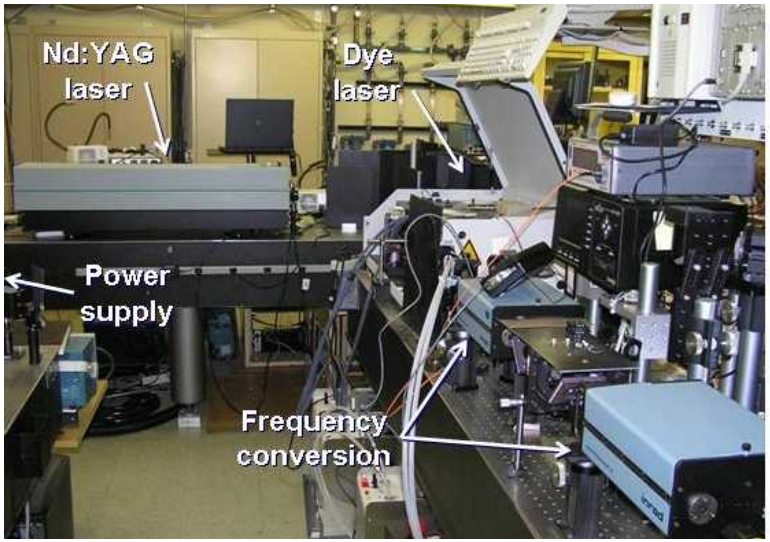
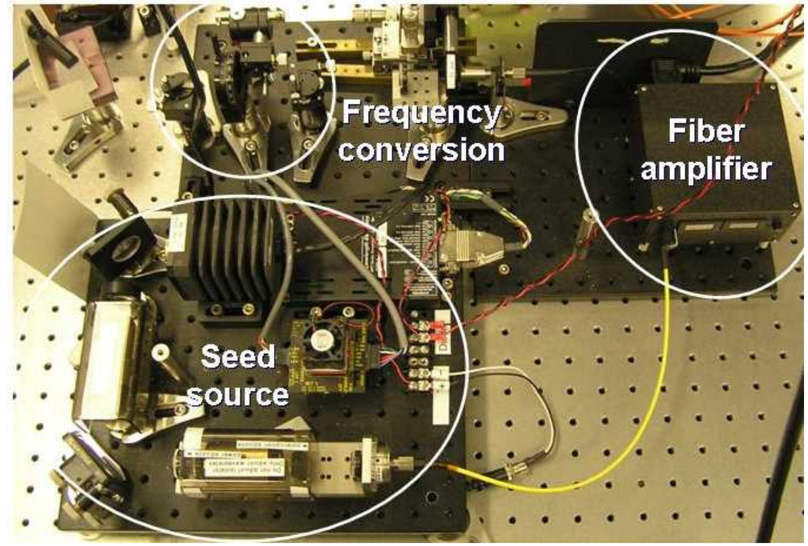
Laboratory Laser vs. Compact Laser





Laboratory Laser	Compact Laser
Tunable (~210 nm)	213 nm
>100 μJ	A few μJs
20-Hz rep rate	~10-kHz rep rate
>2 mW avg.	Few 10's of mW avg.

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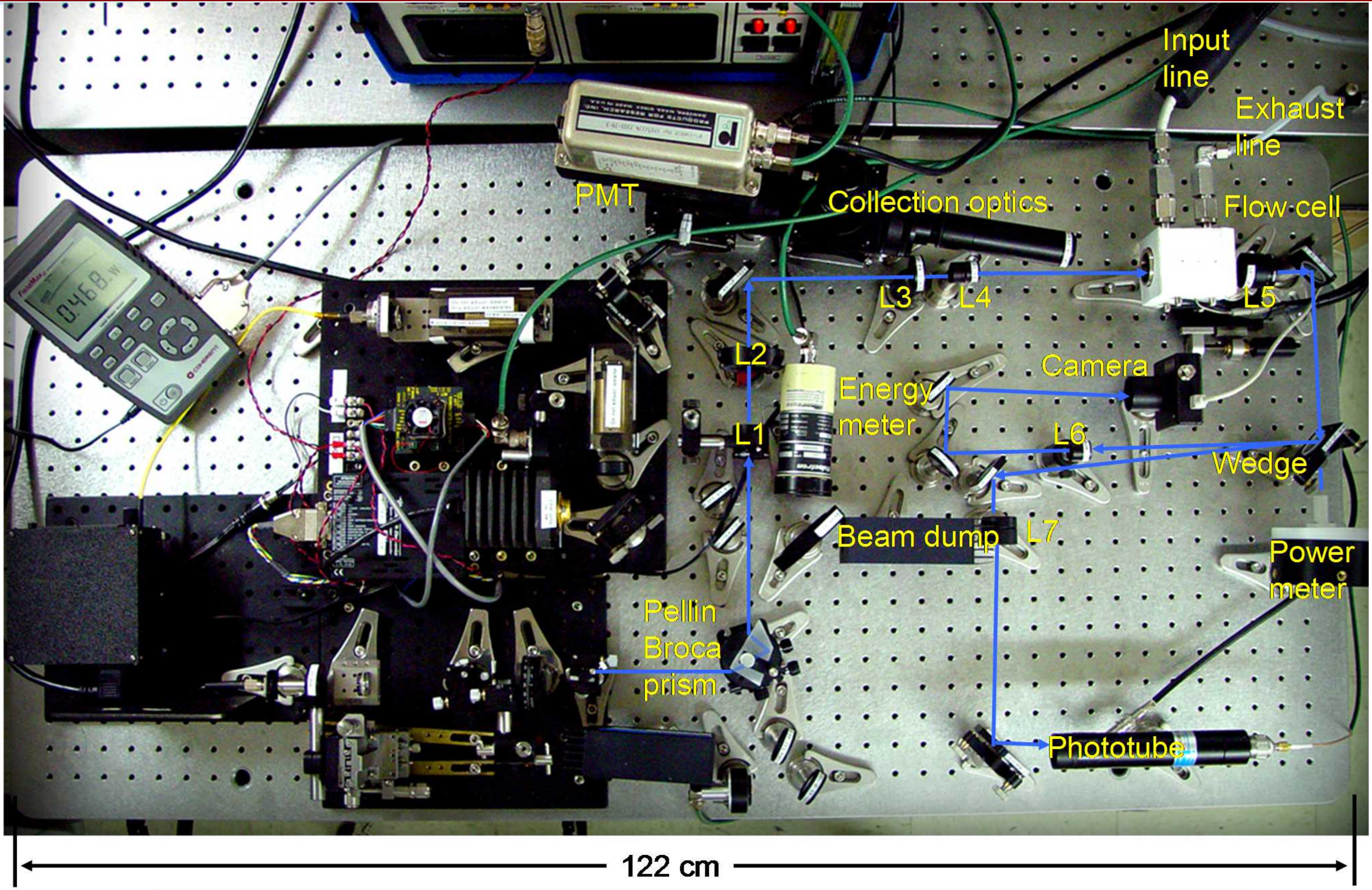
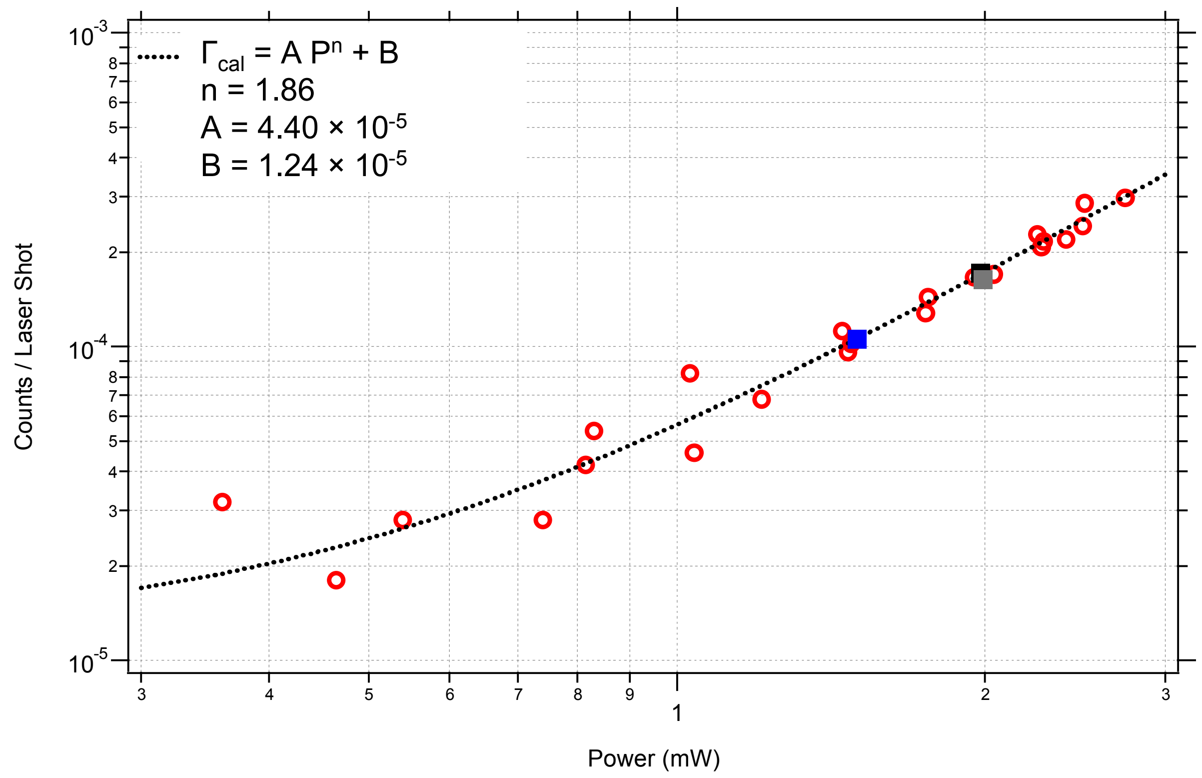
Instrument Cart Optical Layout



Calibration Approach Demonstrated

- Replaced flow cell with calibration cell (with vapor pressure $HgCl_2$)
- Checked for intensity^2 dependence
- Checked for repeatability



Photon-Counting Detection for PFE

- At 0.1 ppb, counts-per-pulse ≈ 10^{-5}
- 10-kHz rep rate, 5-min acquisition time: 3×10^6 laser pulses
- ~30 signal counts will be collected
- Challenge: Background counts

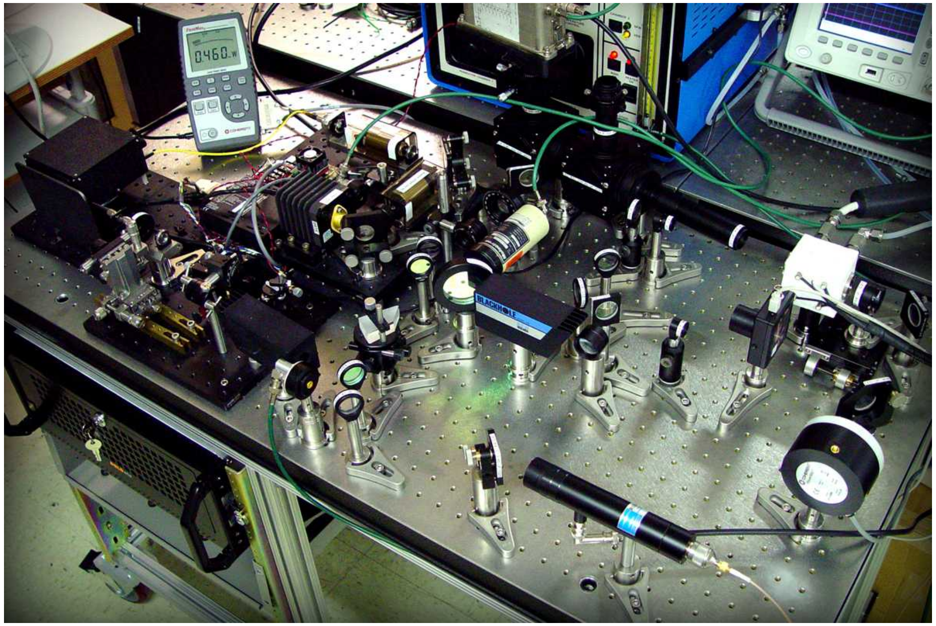
Signal-to-noise ratio = $S/(S+2B)^{1/2}$

S: signal counts

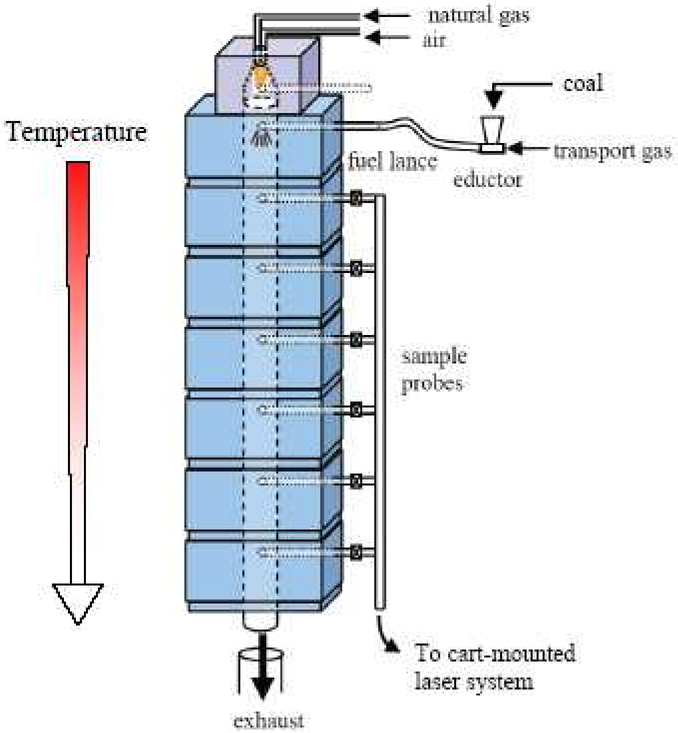
B: background counts

Future Directions

Instrument cart:



Sandia's Multifuel Combustor (MFC):



Experiments are underway to measure the $HgCl_2$ content of coal burned in Sandia's MFC.

Source: C.R. Shaddix and A. Molina, "NOx formation in laboratory investigations of oxy-coal combustion," Fall meeting of the Western States Section of the Combustion Institute, 2007