# Development of a Real-Time Speciating Mercury Emissions Monitor


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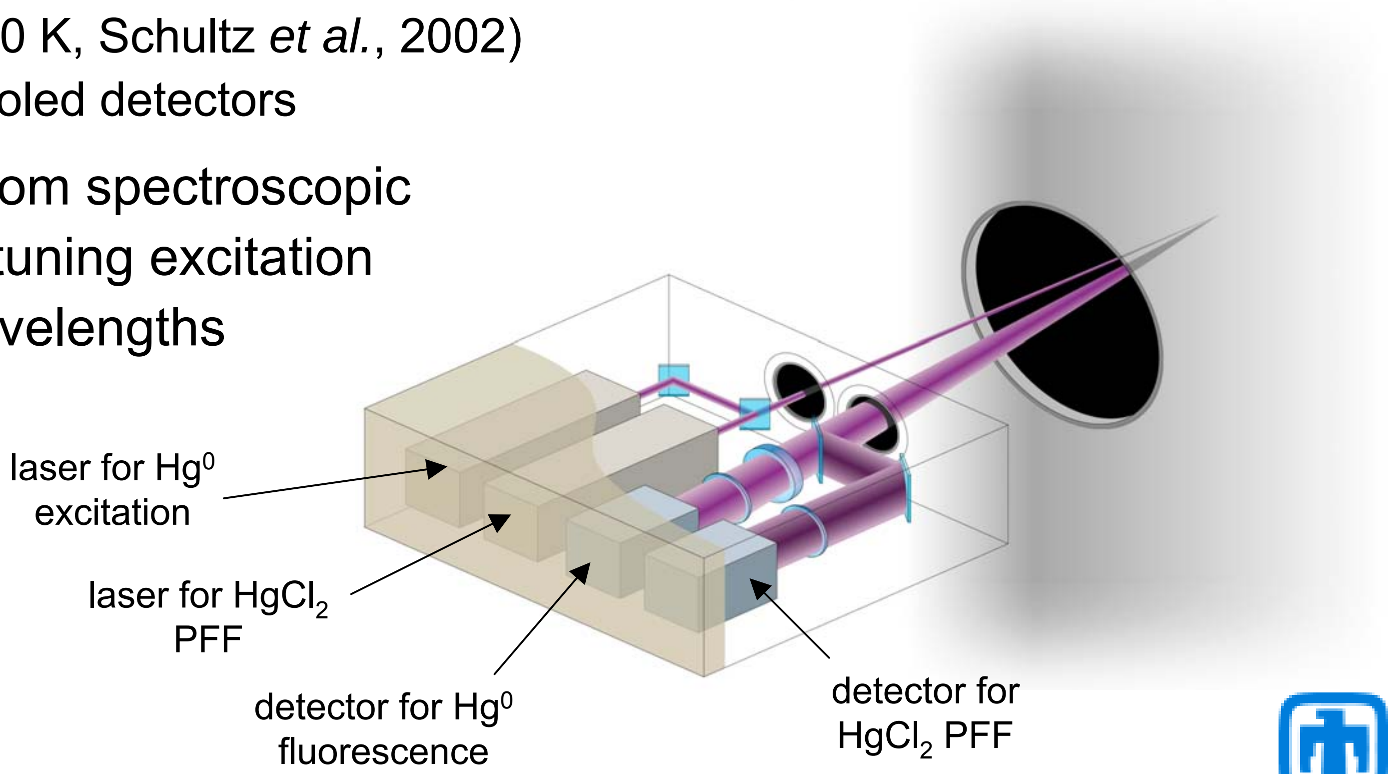
# The Mercury Problem

- Mercury emissions pose the greatest toxic metal risk
- Mercury emissions arise primarily from:
  - Coal-fired power plants
  - Municipal waste combustors
  - Medical waste incinerators
- Vapor-phase mercury exists in elemental and oxidized forms (predominantly $HgCl_2$)
- Reduction of mercury emissions requires species specific cleanup techniques:
  - $Hg^0$: removed with activated carbon sorbent (costly)
  - $Hg^{2+}$: water soluble, removed by wet scrubbers

Need a quantitative, real-time detection instrument that can speciate mercury

# Fluorescence Detection for Speciating Mercury

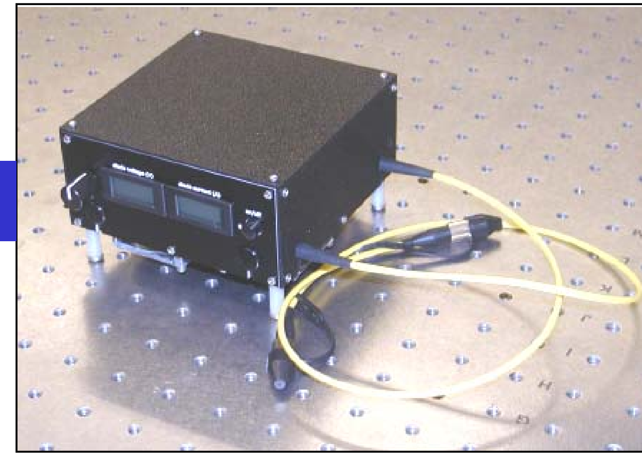
- Employ dual excitation sources and detection elements to quantify $Hg^0$ and $HgCl_2$ emissions
  - $Hg^0$: resonance laser-induced fluorescence (LIF) detection
  - $HgCl_2$: photofragment fluorescence (PFF) detection
- Use UV wavelengths
  - minimize atmospheric absorption of laser excitation (negligible absorption of $\lambda$ > 190 nm at 370 K, Schultz *et al.*, 2002)
  - sensitive, uncooled detectors
- Reduce effects from spectroscopic interferences by tuning excitation and detection wavelengths



# Project Plan

**Spectroscopy:** Develop fluorescence detection of $Hg^0/HgCl_2$

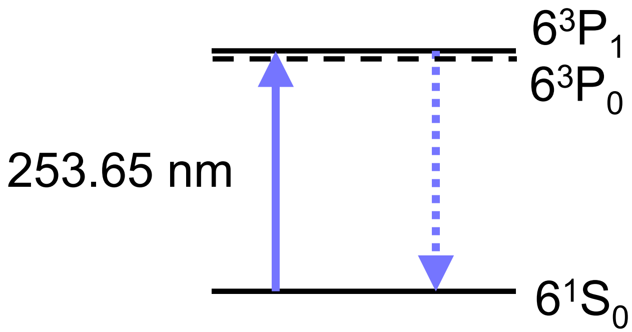
**Laser Advancement:** Develop broadly tunable, fiber-based, UV laser system



**Breadboard Sensor:** Construct and deploy $Hg^0/HgCl_2$ monitor

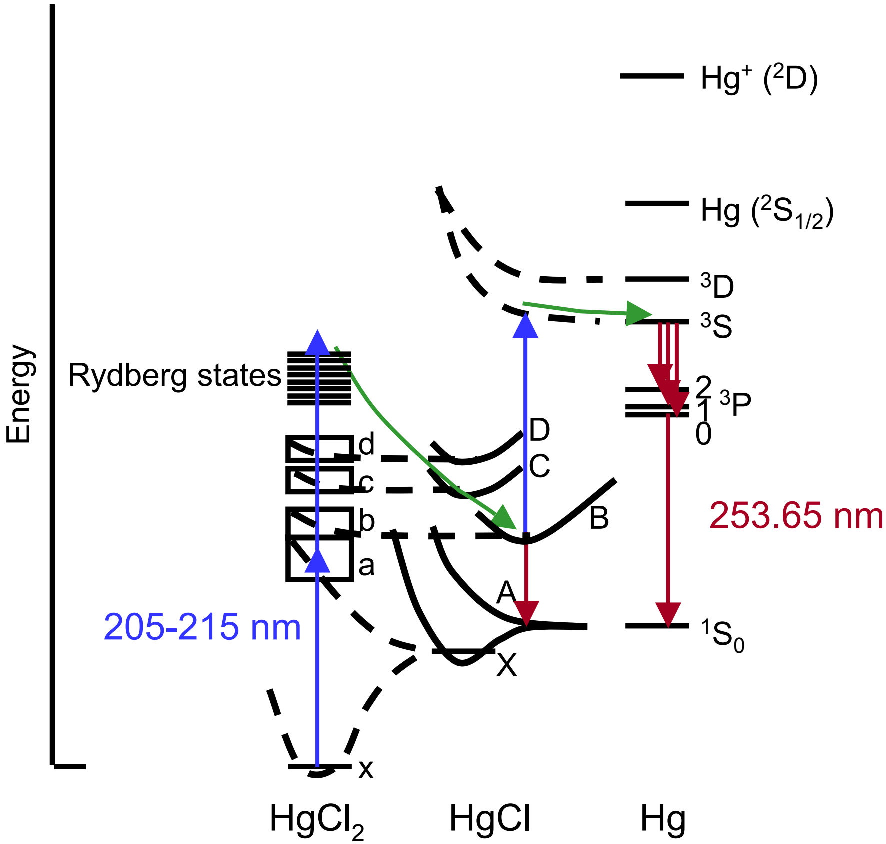
# Resonance LIF of $Hg^0$: $6\ ^3P_1 \rightarrow 6\ ^1S_0$ Transition

- Excite and detect fluorescence at same wavelength:




- Simple implementation: single laser required
- Filter needed to reduce Rayleigh and Mie scattering
- Electronic quenching to metastable $^3P_0$ state results in fluorescence quantum yield to $\sim 10^{-2} – 10^{-3}$

# Probable $HgCl_2$ PFF Mechanism




Potential energy curves adapted from Whitehurst and King, 1987

- Two photon excitation of $HgCl_2$ to Rydberg state:

  $HgCl_2$ (x $^1\Sigma_g^+$) + 2$h\nu_{laser}$ → $HgCl_2$ (Rydberg)

- Dissociation of $HgCl_2$ yields B state HgCl products:

  $HgCl_2$ (Rydberg) → HgCl (B $^2\Sigma^+$) + Cl ($^2P_{3/2}$)

- One photon excitation of HgCl produces excited atomic mercury:

  HgCl (B $^2\Sigma^+$) + $h\nu_{laser}$ → Hg* + Cl ($^2P_{3/2}$)

- Hg* fluoresces at several transitions, emission monitored at 253.65 nm:

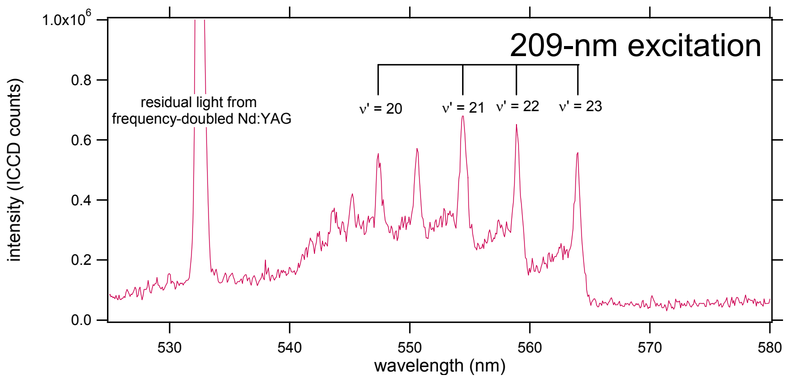
  Hg* (6 $^3P_0$) → Hg (6 $^1S_0$) + $h\nu_{emission}$

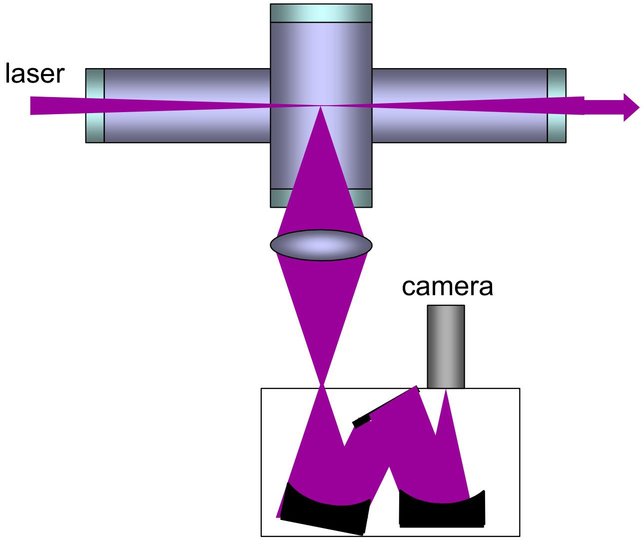
- Note that HgCl fluorescence competes with photoexcitation:

  HgCl (B $^2\Sigma^+$) → HgCl (X $^2\Sigma^+$) + $h\nu_{emission}$

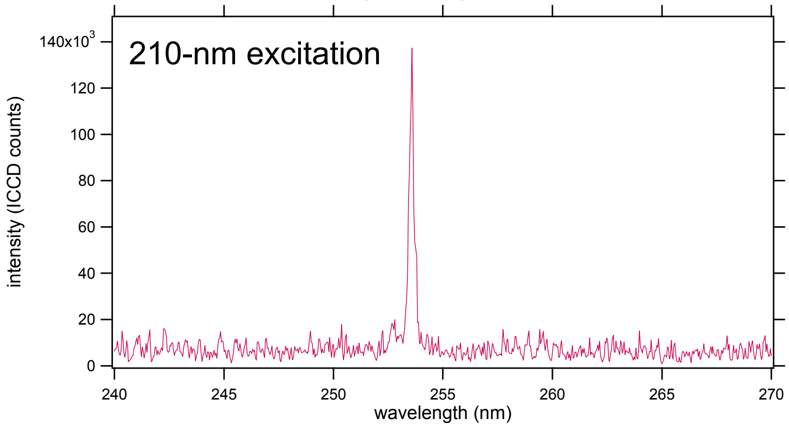
# Spectroscopy and Diagnostic Potential of PFF

Fluorescence from HgCl* B-X at low pressure (6 torr)

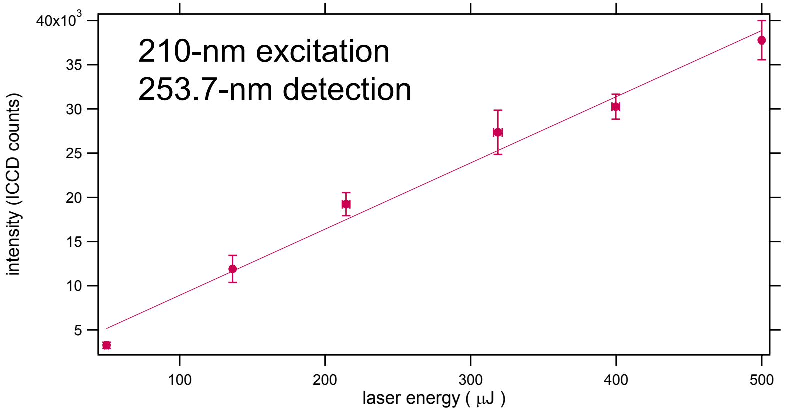



Fluorescence from Hg* $6^3P_1 \rightarrow 6^1S_0$ at atmospheric pressure




Dependence on Laser Energy

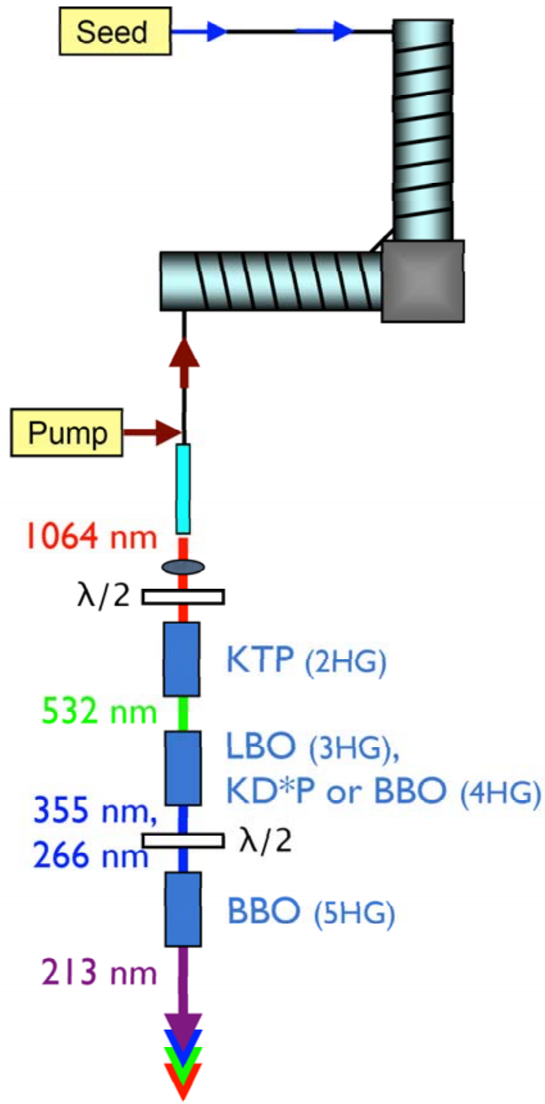


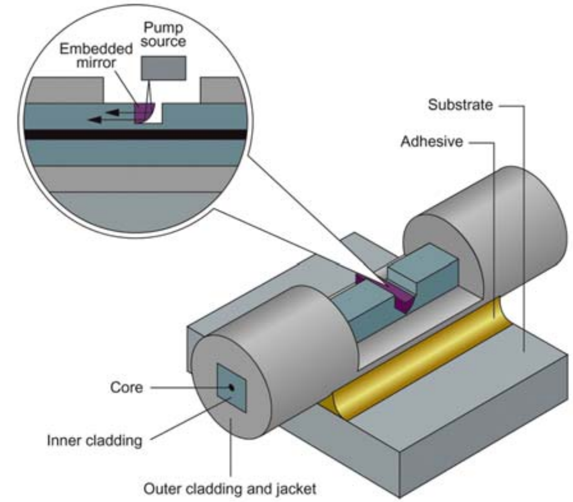
# Quantifying Technique / Minimizing Interferences

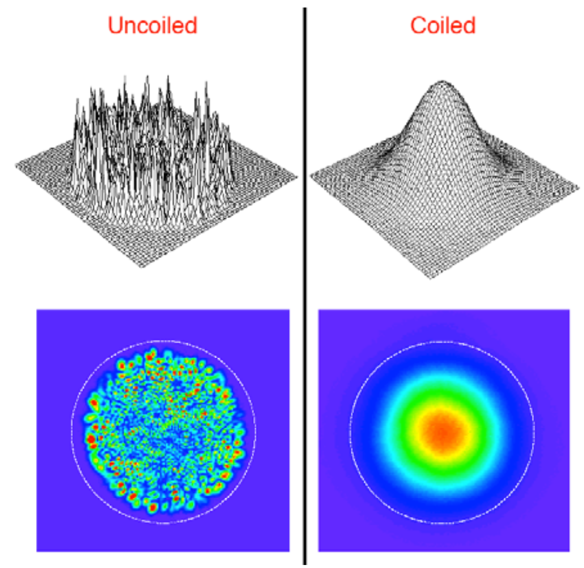
- Evaluate effects of flue gases on PFF: 74% $N_2$, 6% $O_2$, 12% $CO_2$, 8% $H_2O$
- Potential spectroscopic interferences to investigate: $SO_2$, NO, and $NO_2$
- Incorporate narrow filters (5 nm) to reject majority of fluorescence signal from species other than Hg*
- Tune excitation wavelength for $HgCl_2$ away from interferences
- Employ multi-wavelength detection scheme:
  - Use two filters that transmit different spectral regions: on and off the Hg fluorescence peak
  - Subtract "off" signal from "on" signal to account for fluorescence from interference species
- Determine optimal excitation and detection wavelengths

# Fiber Amplifiers

- If a fiber-core is doped with a rare-earth ion, the ion can be optically pumped.
- Fiber becomes an optical amplifier rather than a passive “light pipe.”
- Two Sandia/NRL developments:
    1) launching diode light into fiber with embedded mirror
    2) coiled fiber for power scaling

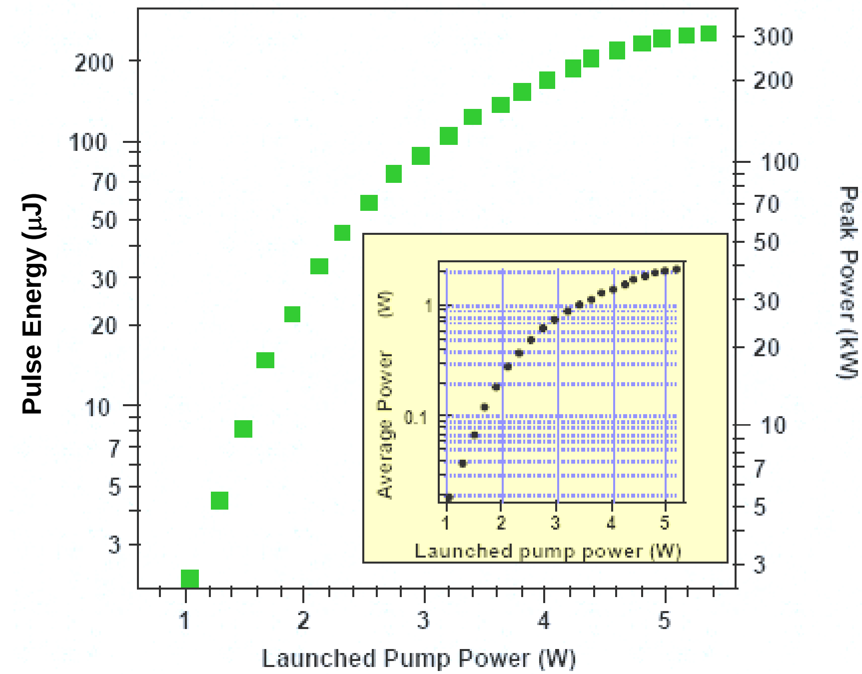


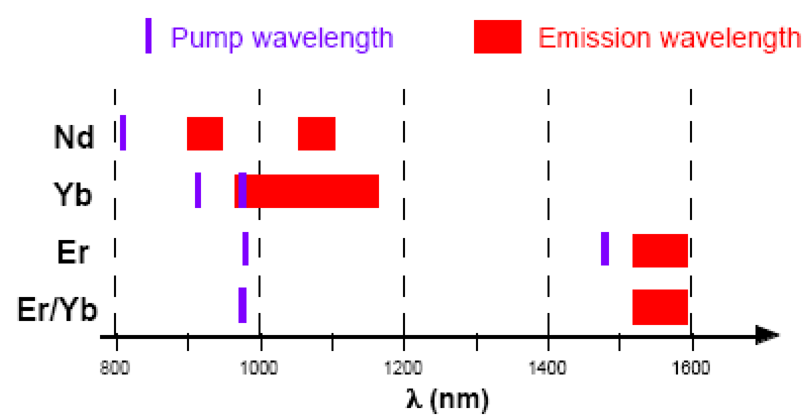



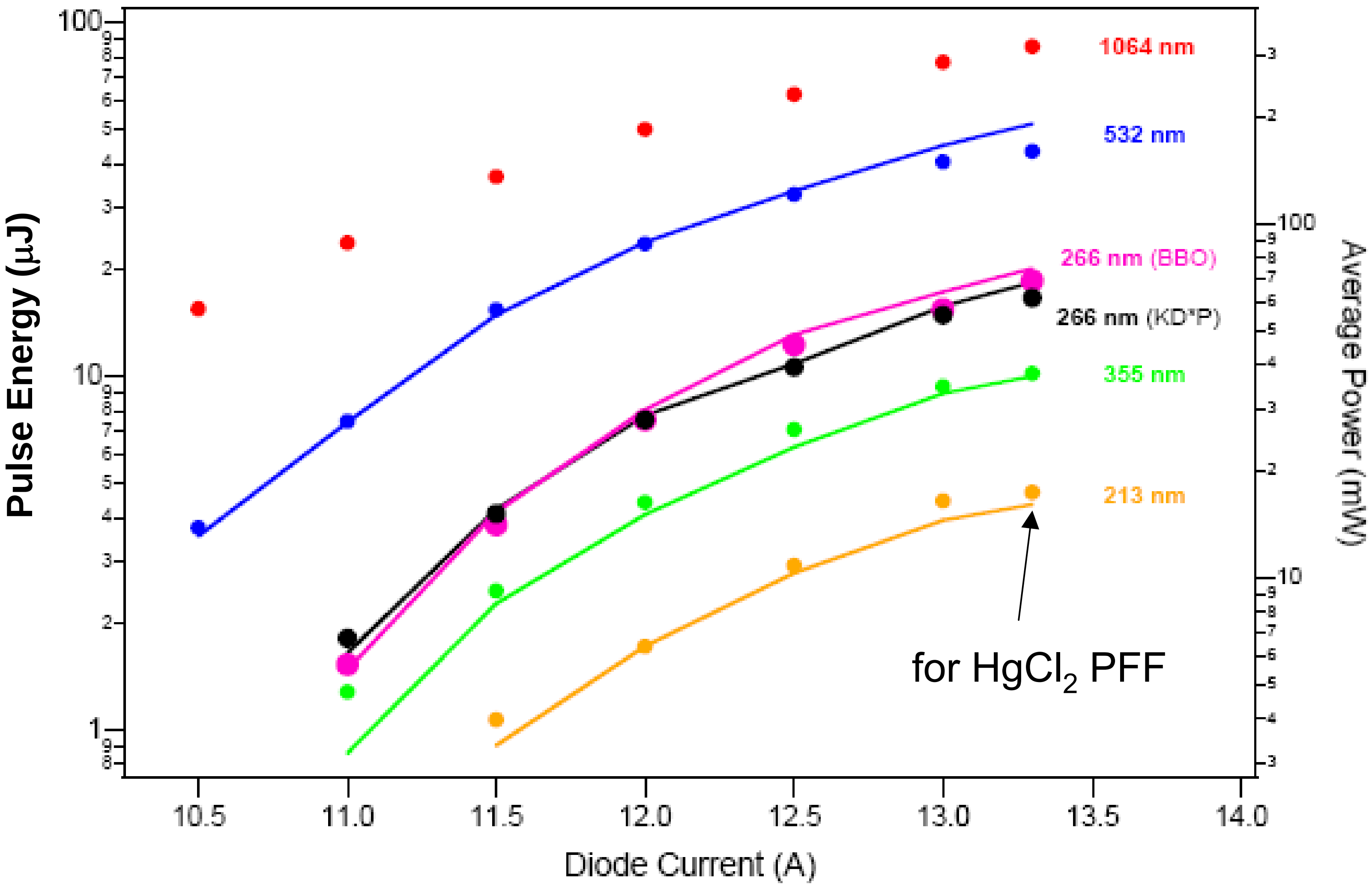
# Fiber Amplifier Characteristics

- Compact and rugged
- Diffraction-limited beam quality
- High efficiency: 39% electrical-to-optical
- Insensitive to:
  - Temperature
  - Mechanical fluctuations
  - Optical power level
  - Aging of laser system
- Pumped with reliable, low-cost diode lasers operating at room temperature
- Sealed, alignment-free optical system
- Broad wavelength coverage



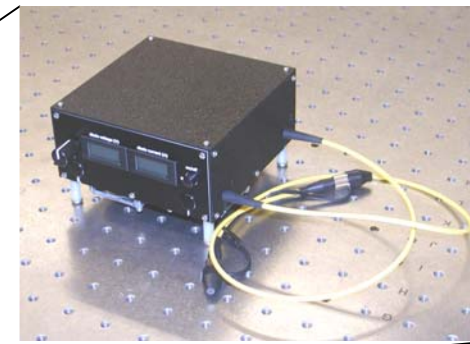



# Fiber Amplifier Output and Harmonics



# Fiber Laser Systems Make Optical Sensors Practical


Sandia Fiber Amplifier



| | | |
|---|---|---|
| Output power (266 nm): | 200 mW | 100 mW |
| Weight: | 250 lb (laser, power supply, chiller) | 2 lb |
| Volume: | 16,000 $in^3$ | 60 $in^3$ |
| Input power: | 2000 W | 10 W |
| Cooling unit: | water/air heat exchanger | none (air cooled) |