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Pump-Probe Detection of Surface-Bound Organophosphonate Compounds

Thomas A. Reichardt, Scott E. Bisson, Jeffrey M. Headrick, Roger L. Farrow, and Thomas J. Kulp

Sandia National Laboratories

P. O. Box 969, MS 9056

Livermore, CA 94551

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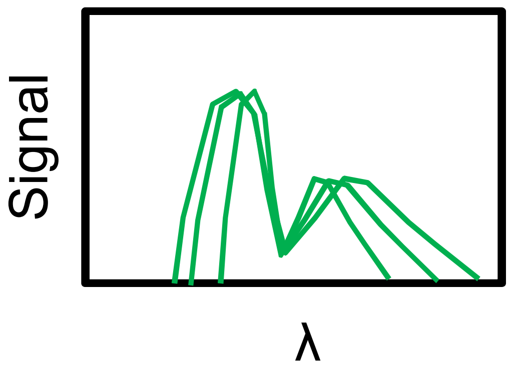
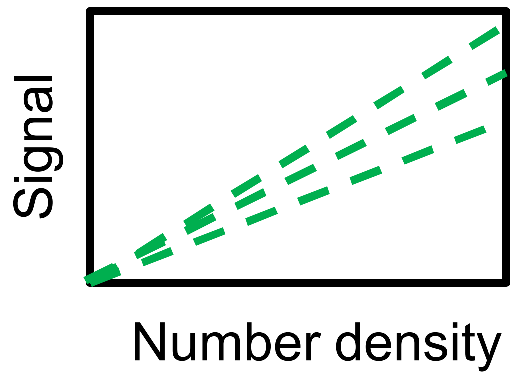
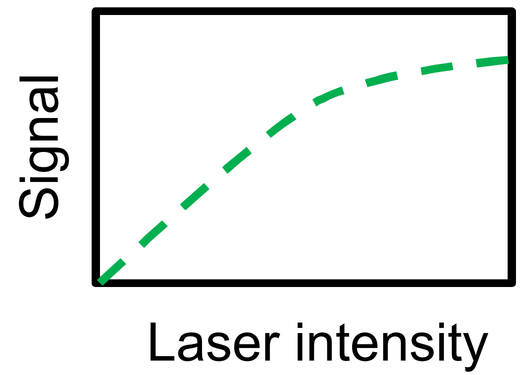
Photofragmentation Detection: Sensitivity and Specificity

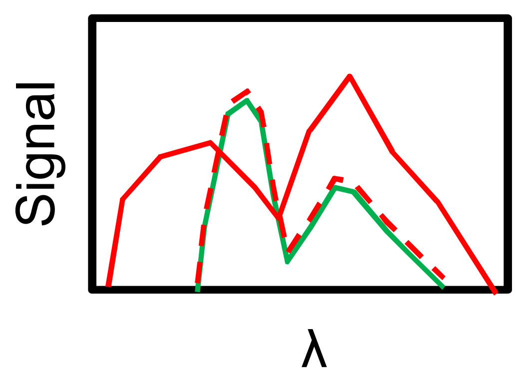
- **Spectral features unsuitable for direct optical probing.**
- **However, photofragmentation can produce PO.**
- **Sensitivity**





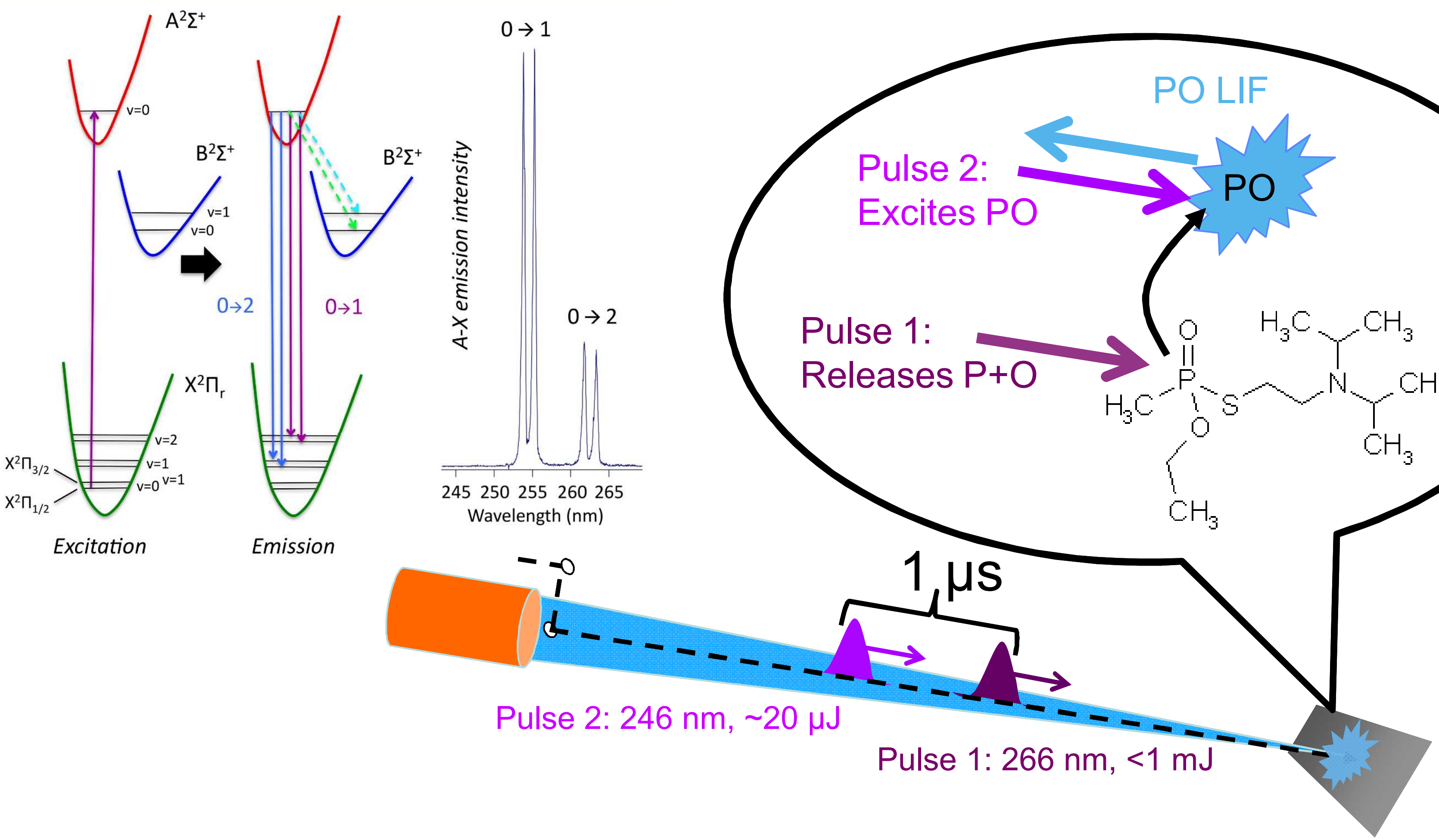


- **Specificity**



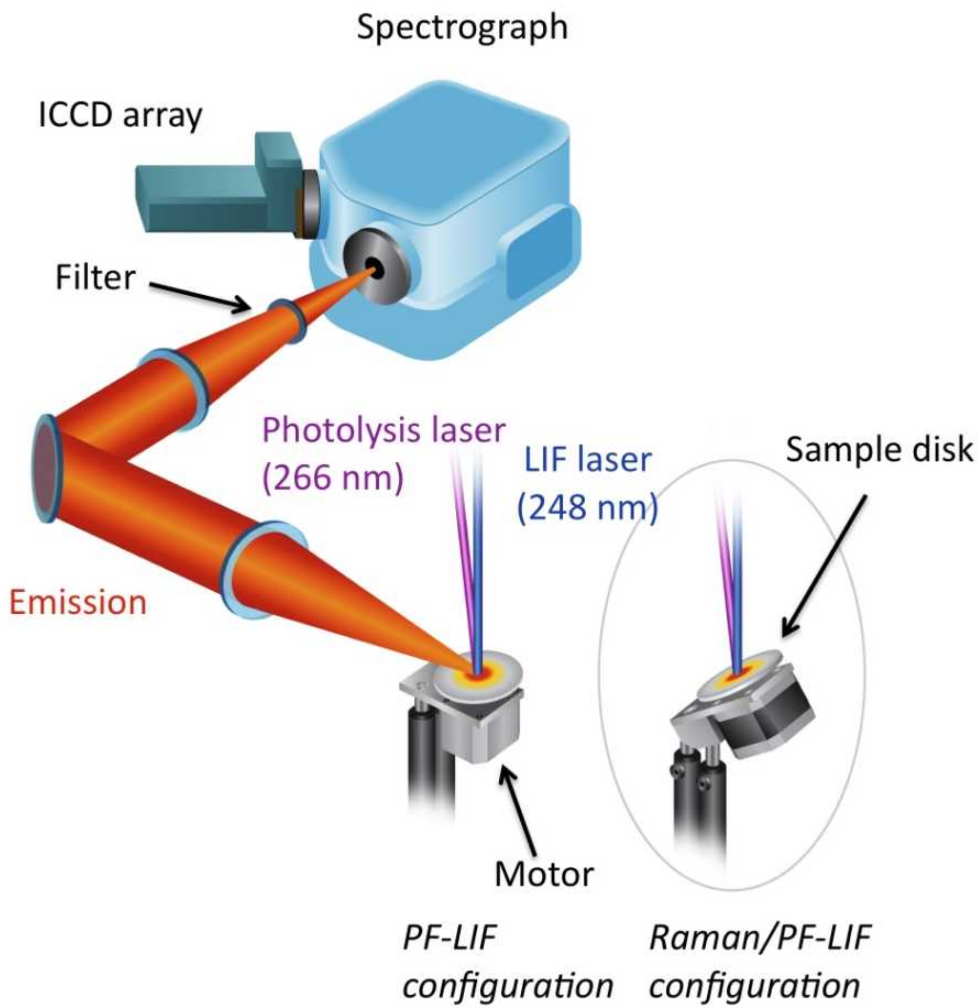
- **Interferences**
- **Matrix effects**

Photofragmentation Detection of *Vapor-Phase* Organophosphonates



Long et al. (1986) and Shu et al. (2000) demonstrated PF-LIF for vapor-phase organophosphonates.

Detection of *Surface-Bound* Organophosphonates



- **Two substrates thoroughly investigated**
  - **Aluminum (highly conductive, low porosity)**
  - **Concrete (non-conductive, high porosity)**
- **Rotate sample and acquire single-pulse-pair spectra**
- **Unmix the spectra into target and background**

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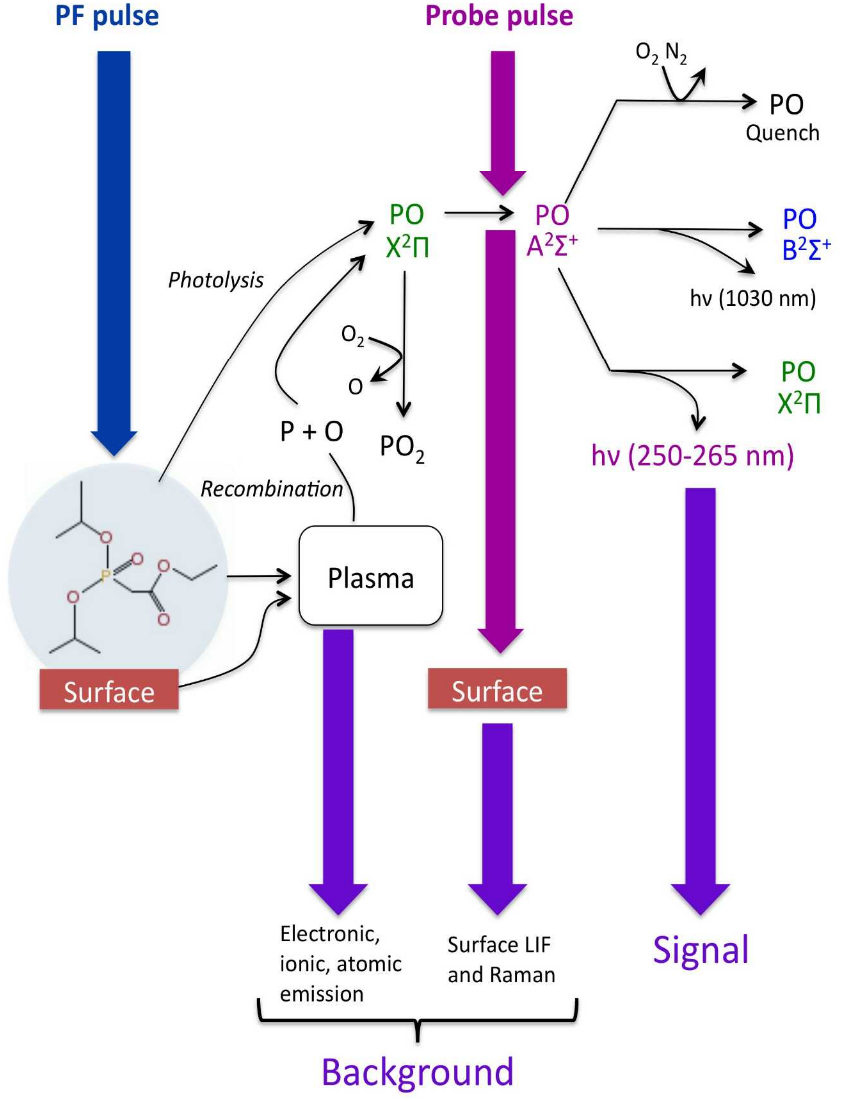
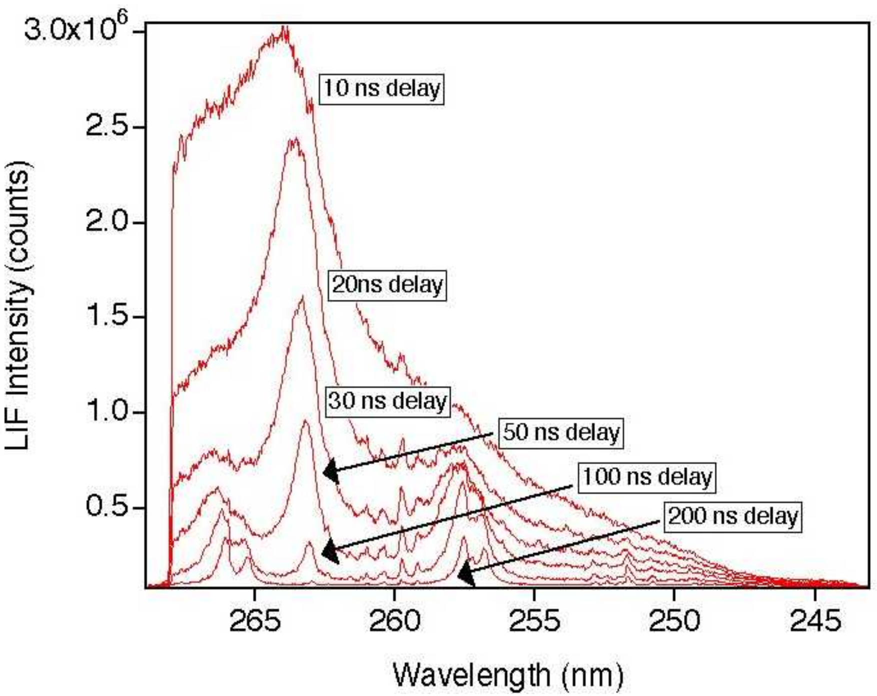
Temporal/Spectral/Spatial Studies of PO Formation



Spectrally resolved PO LIF at different probe delays



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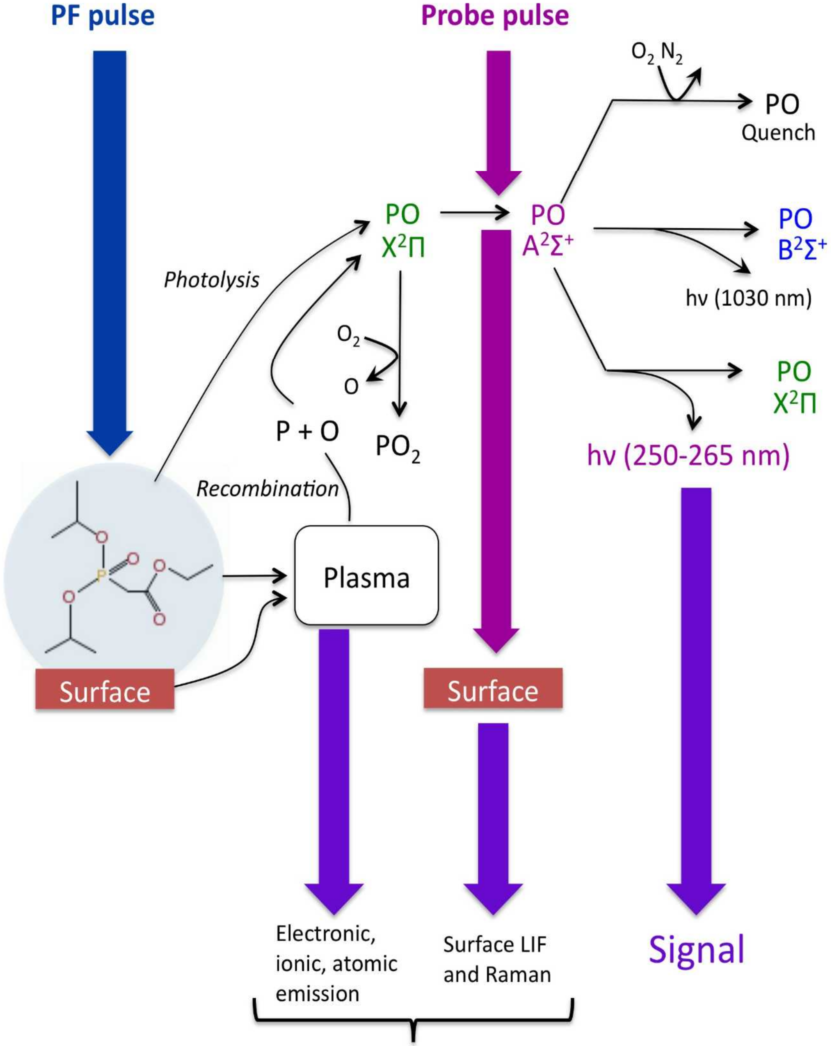
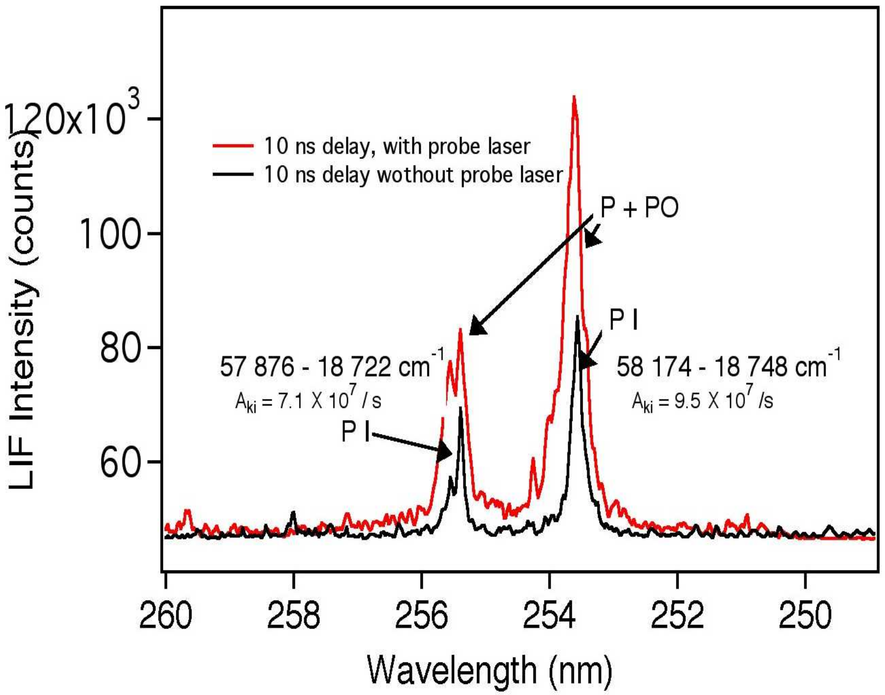
Temporal/Spectral/Spatial Studies of PO Formation



LIBS of P observed at short probe delays



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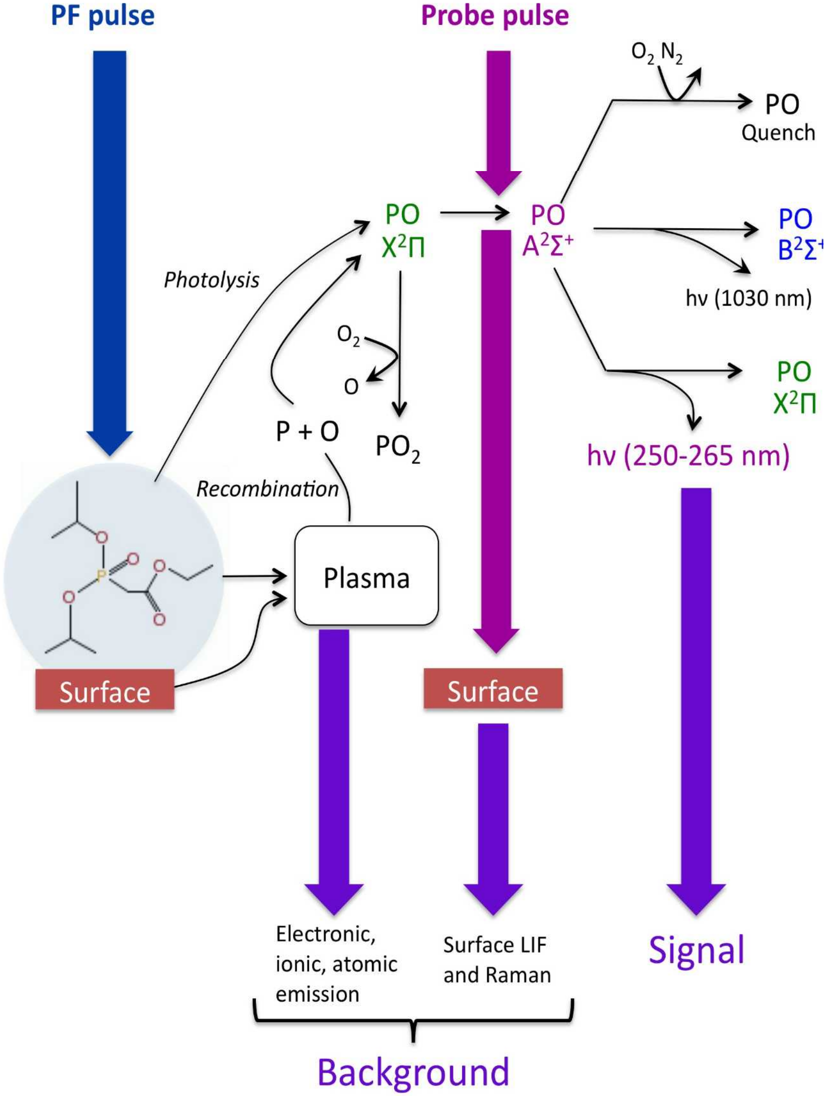
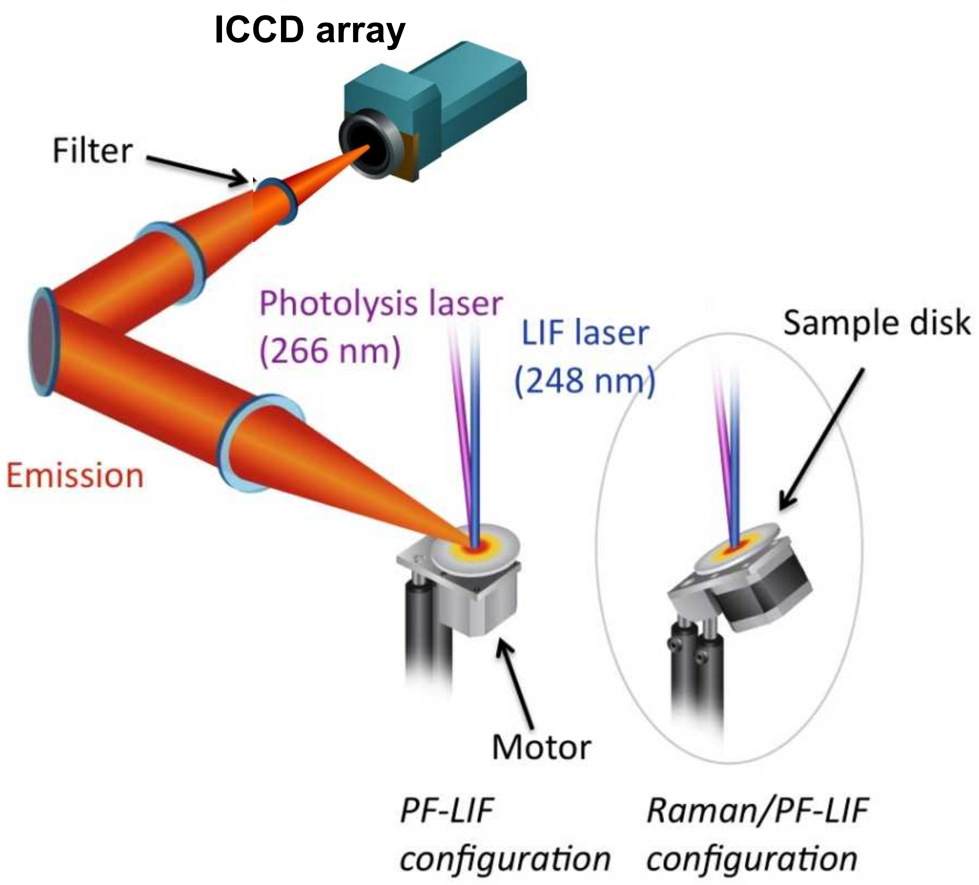
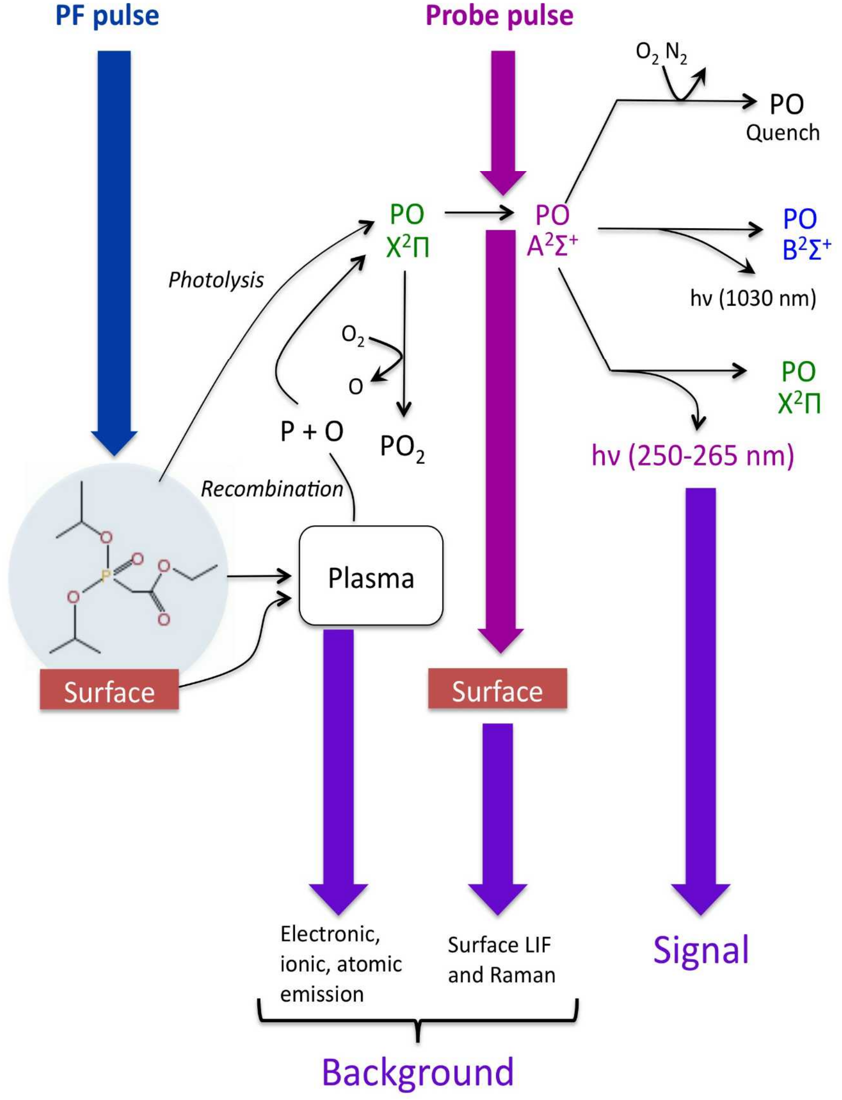
Temporal/Spectral/Spatial Studies of PO Formation



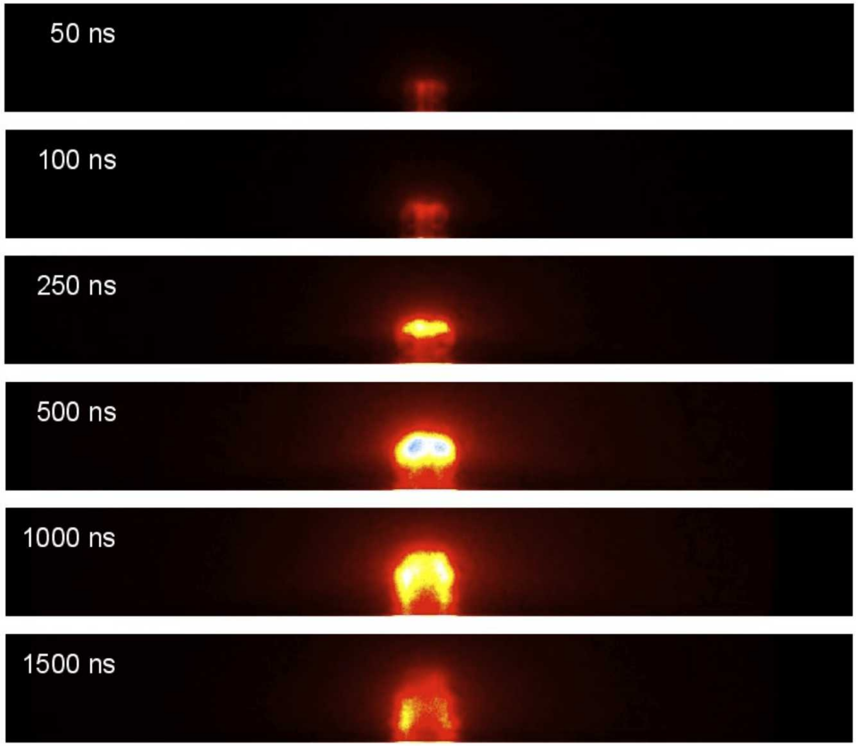
Modified instrument for planar laser-induced fluorescence (PLIF)



Temporal/Spectral/Spatial Studies of PO Formation



Spectrally integrated PO PLIF at different probe delays



Conclusion: PO is likely formed through recombination of P and O

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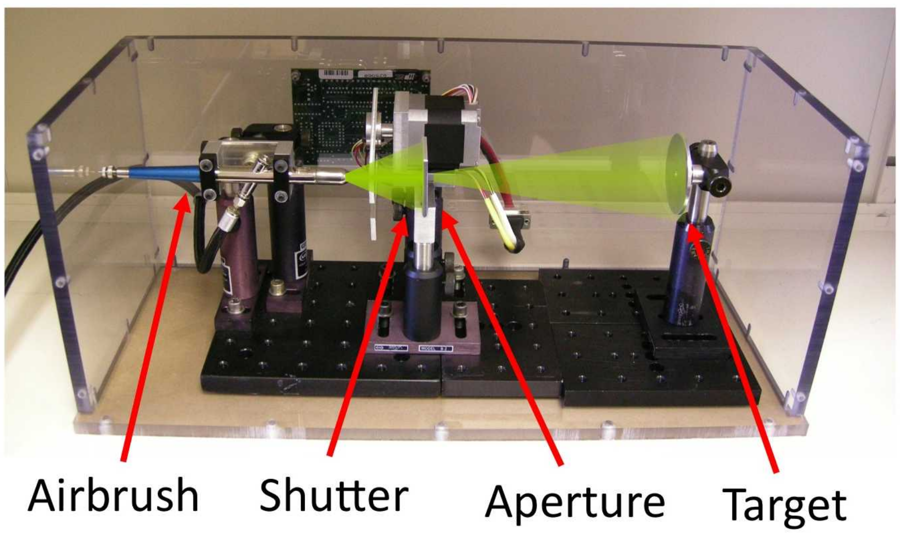
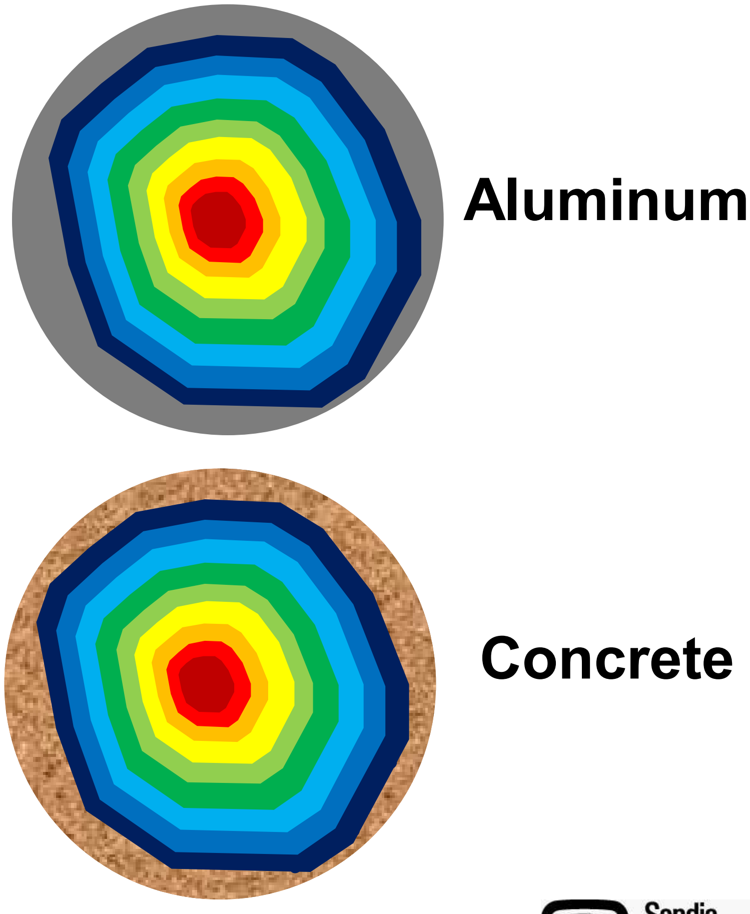
Determine Detection Limits by Unmixing Target and Background Signals

- DIPP was deposited with apertured airbrush
- Average deposition measured gravimetrically (~1 mg lower limit)

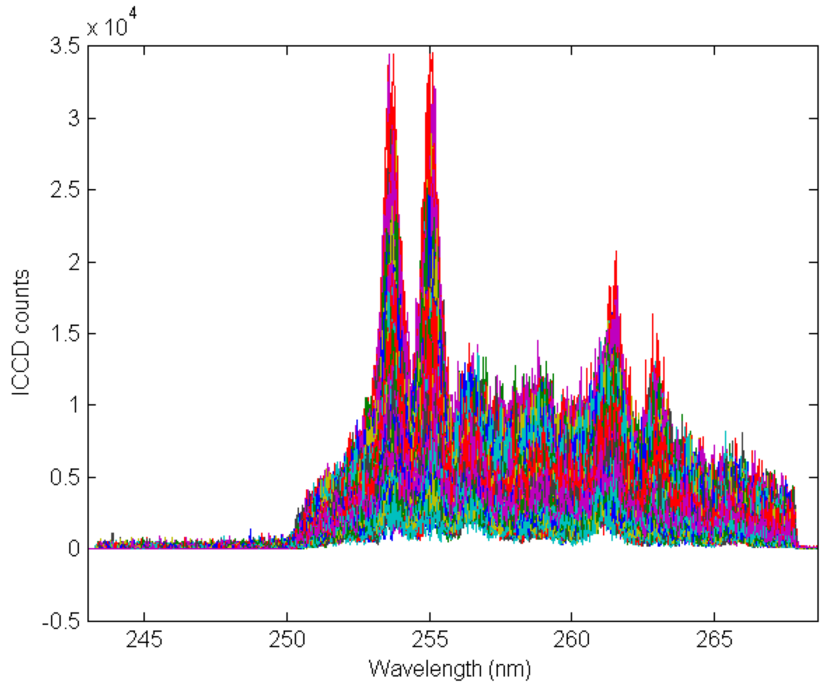




Analysis of Single-Pulse-Pair Spectra

- 600 single-pulse-pairs were acquired for each run
- Sandia's runAxsia software performs Multivariate Curve Resolution (MCR)
- # pure components = 2
  - 1 signal, 1 background
- Solved $D = CS^T + E$

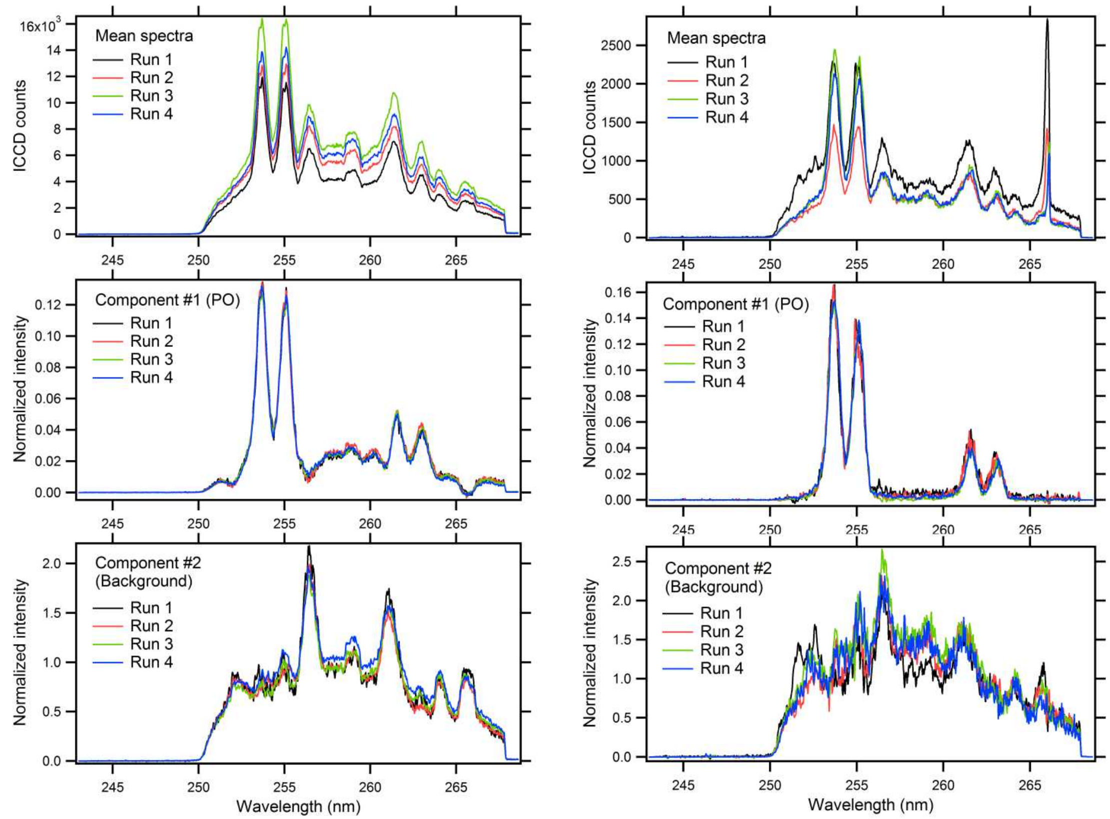
Error
Acquired spectra
Concen-trations
Pure component spectra



600 single-pulse-pairs for aluminum substrate

- Alternating least squares to minimize E: $\hat{C} = DS^{T+}$, $\hat{S}^T = \hat{C}^+D$

Multivariate Curve Resolution
Pure Component Spectra



Aluminum substrate **Concrete substrate**

A background component co-varies with the PO fluorescence on aluminum, but not on concrete.

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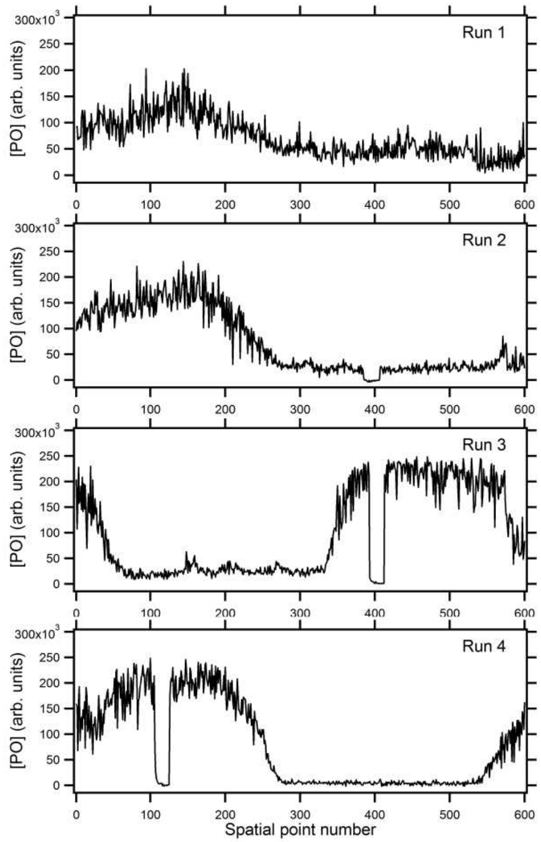
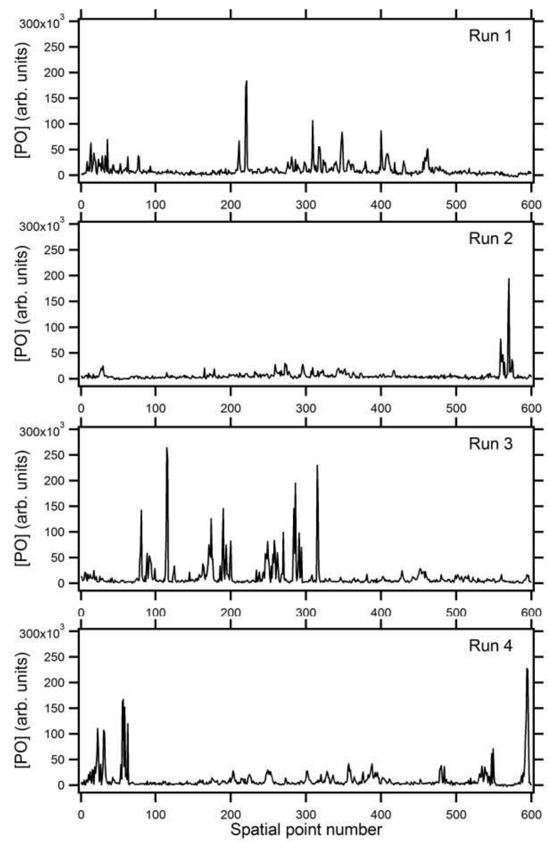
Multivariate Curve Resolution
Relative Concentrations



Aluminum substrate



Concrete substrate

The DIPP signal is spatially continuous on aluminum, but not on concrete.

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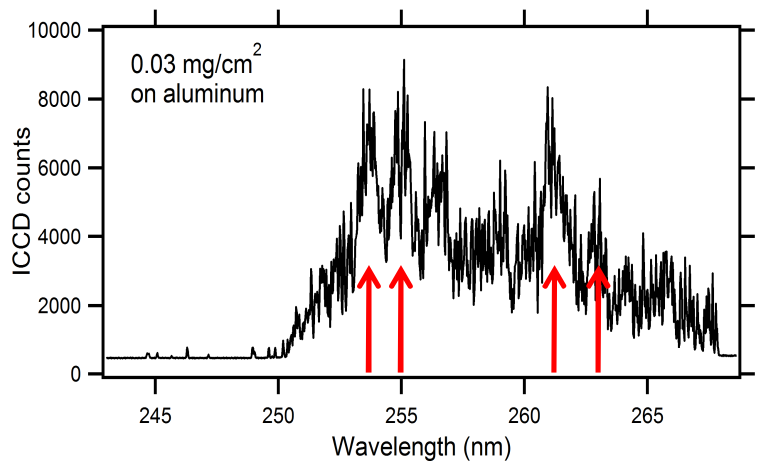
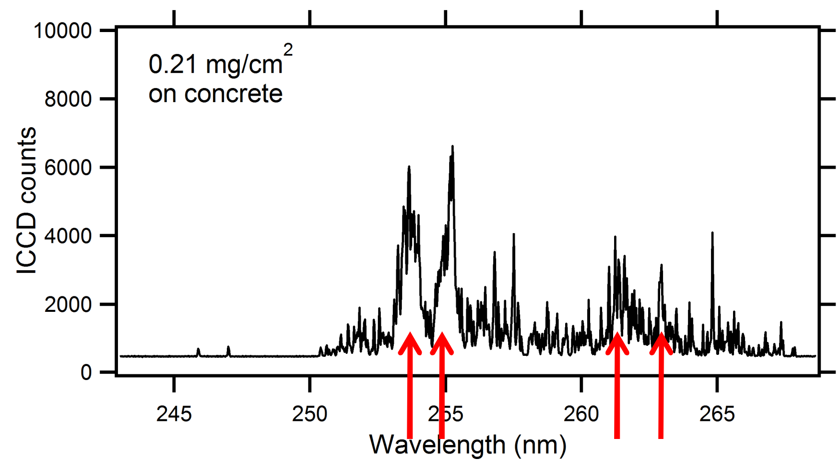
Calculating the Single-Pulse-Pair Detection Limit

- Converted to photoelectrons: detection limit at SNR = 20

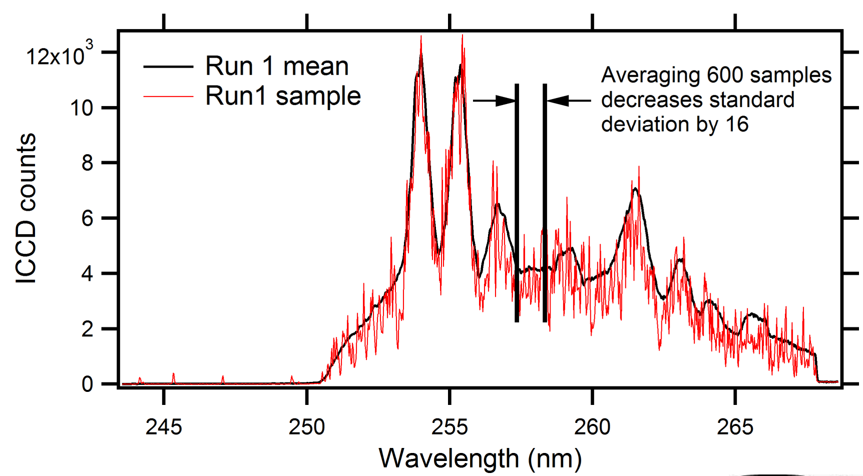
30 μg/cm² on aluminum



210 μg/cm² on concrete



- Temporal averaging could improve detection limit
- Std. dev $\propto (2.3/N)^{1/2}$
- Pulse energies compatible with >10 kHz sources
- Averaging + fast response



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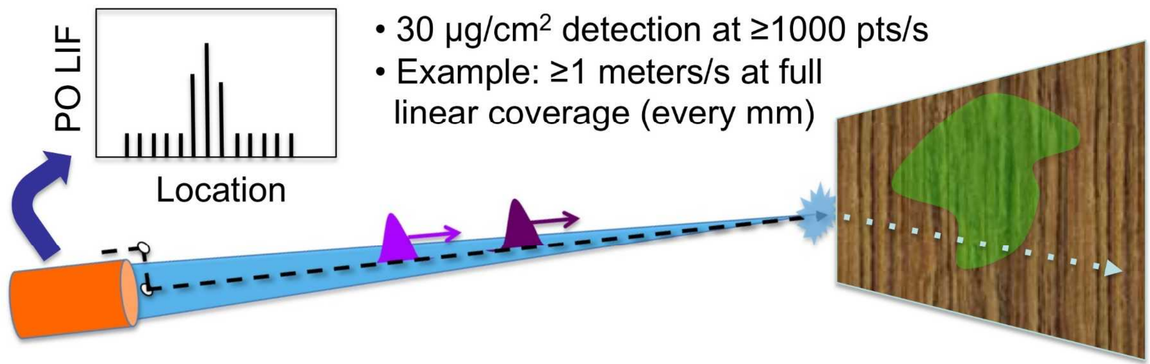
Conclusions

- **For surface-bound organophosphonates, detected PO likely results from P recombining with O**
  - **Implications for specificity**



- **Single-pulse-pair detection limit depends on substrate**
  - **Implications for quantitatively assessing detection methods**
- **Evaluating single-pulse-pair data provides some knowledge of backgrounds**
  - **Differences noted between aluminum and concrete backgrounds (not apparent from averaged data)**

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