THE OHIO STATE UNIVERSITY

Sensitivity enhancement for trace detection of carbonyls by submillimeter wave spectroscopy

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National Ambient Air Monitoring Conference, St. Louis, MO August 10, 2016

Introduction

<u>Submillimeter wave (SMMW) spectroscopic gas sensor</u>

- Developed by OSU and Battelle for DARPA
- Exceptional sensitivity, selectivity, and speed
- Adaptable to ambient air monitoring applications
  - Direct detection of formaldehyde, acrolein, NOx, SOx, etc.
  - Simultaneous detection of multiple air pollutants
- Reduce reliance on lab-based sample analysis

Presentation outline

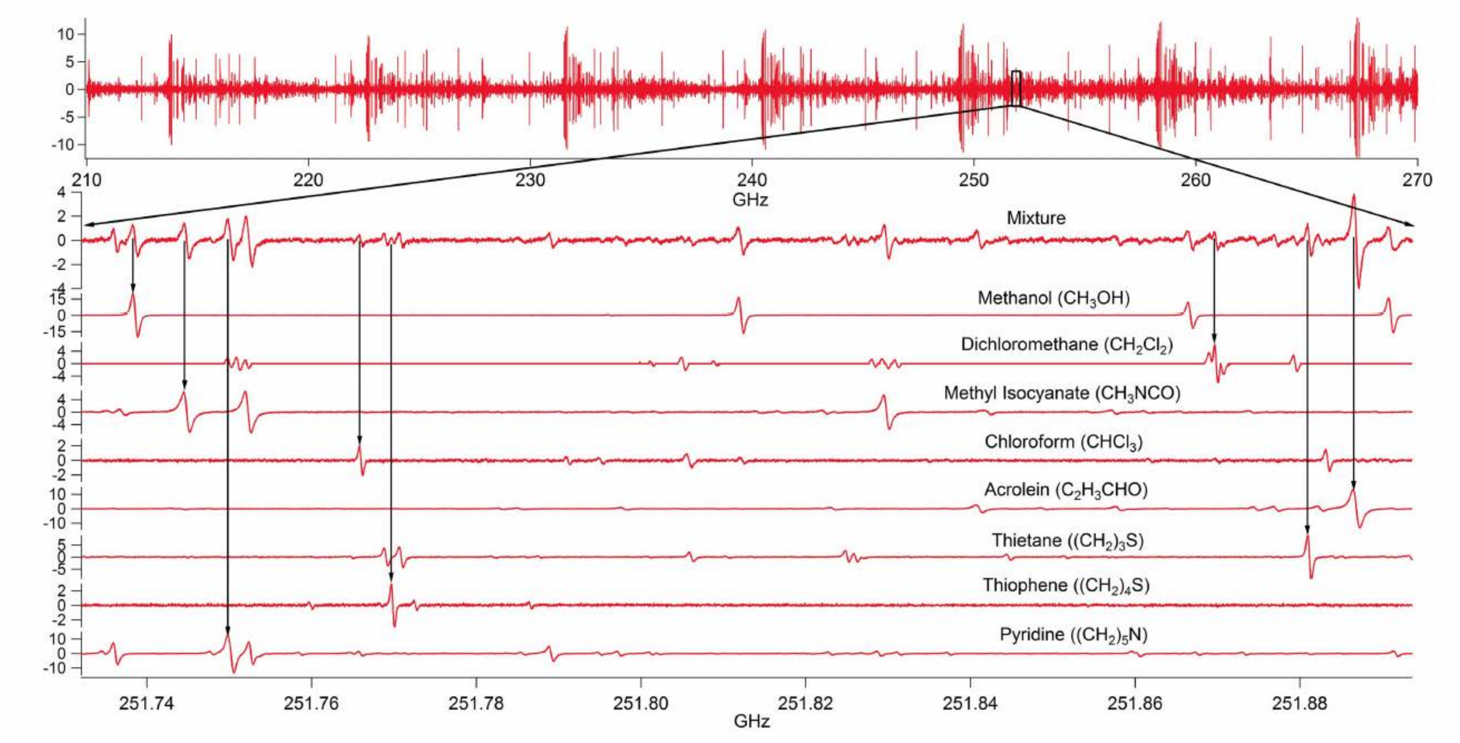
- Background
- Previous work
- Objective of current study
- Optical multipass design and assembly
- System characterization
- Diagnostic spectroscopy measurements
- Next steps

Background

- EPA requires carbonyl detection in ambient air at sub-ppb concentrations
  - Formaldehyde, acrolein, acetaldehyde
- Current field monitoring methods need improvement
- SMMW spectroscopy offers near-real time detection of carbonyls
- Additional research needed to enhance SMMW sensitivity without relying on sorbent-based preconcentration

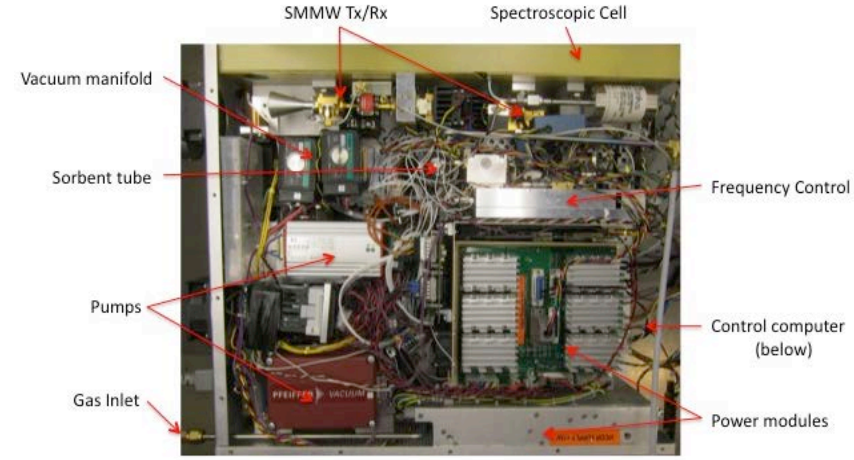
Spectroscopic phenomenology

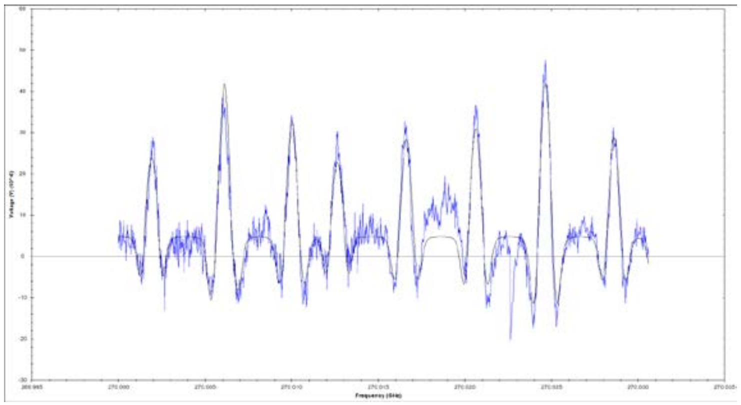
- High resolution rotational spectroscopy
  - Resolves individual spectral lines
  - Optimal sensitivity near Doppler limit (~10 mTorr)



Previous work

- DARPA MACS program
  - Sensitivity: ~ppt (with preconcentration)
  - Selectivity: simultaneous detection of 30+ gases
  - False alarm rate: < 10^{-10}
  - Speed: 10 min
  - Size: 1 cubic foot
- EPA/OAQPS feasibility study
  - Investigate sorbent-free MDL of formaldehyde, acrolein, acetaldehyde
  - Within factor of 200 for formaldehyde MDL





Neese, et al., *IEEE Sensors Journal* vol. 12, pp. 2565-2574, 2012

Detection sensitivity

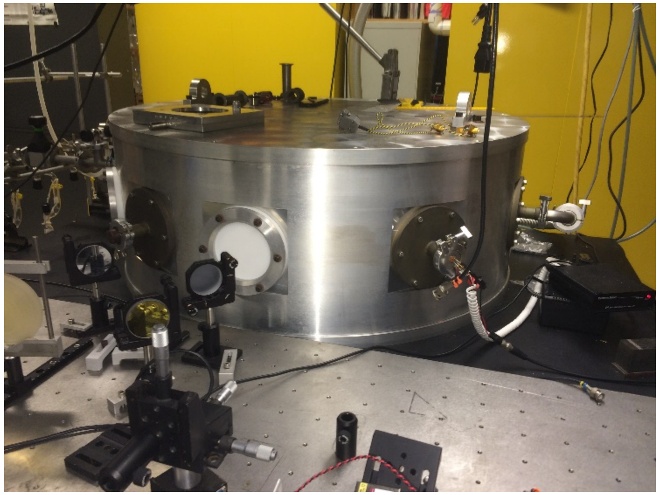
- Inherent molecular absorptivity
- Pressure/number density
  - Preconcentration
- SMMW power
- Signal averaging
- Optical path length

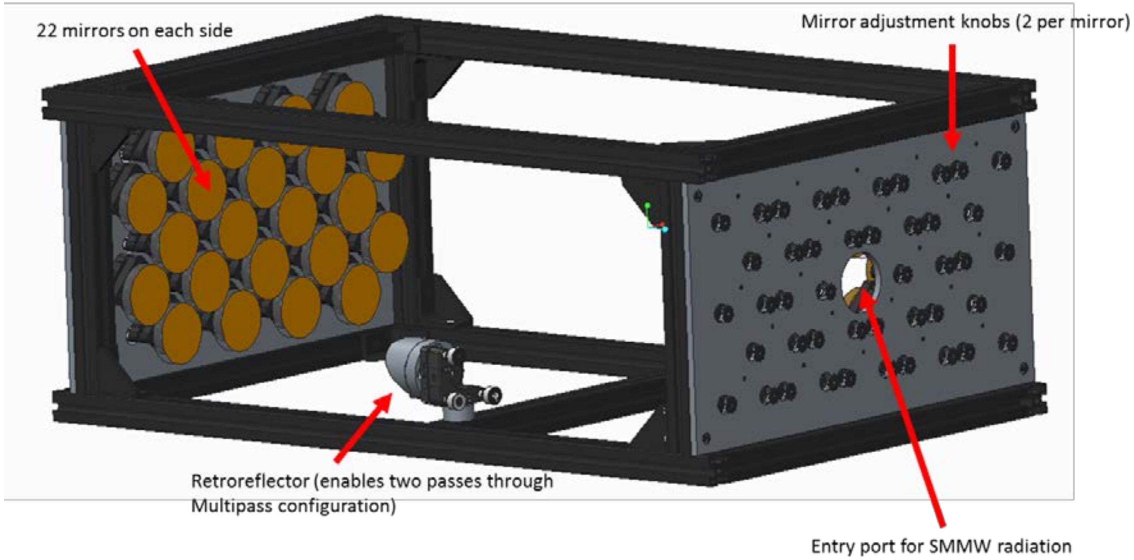
Objective

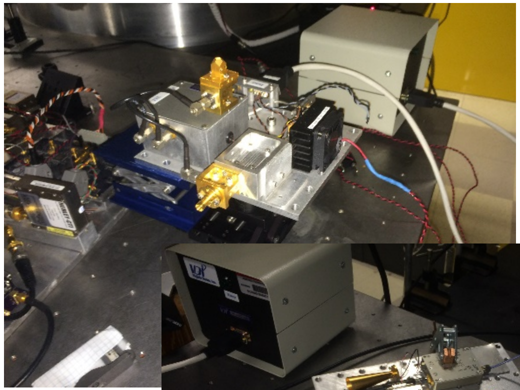
- Develop optical multipass configuration to enhance sensitivity of SMMW spectrometer
  - Focus on carbonyl detection
    - Formaldehyde, acrolein, acetaldehyde
  - Demonstrate gains toward carbonyl minimum detection levels (MDLs)
  - Enable potential sorbent-free operation in a future fielded SMMW system

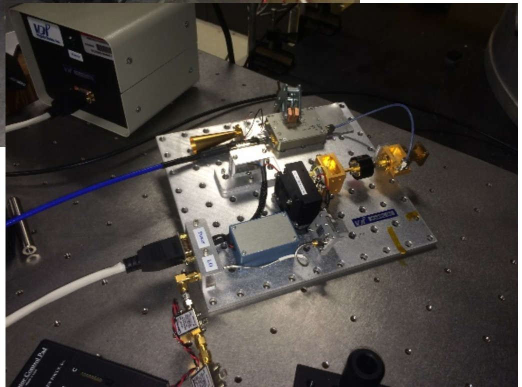
Multipass design considerations

- Multipass vs. White cell
- Polarization
- Vacuum chamber
- Mirror selection
- Proof-of-concept design

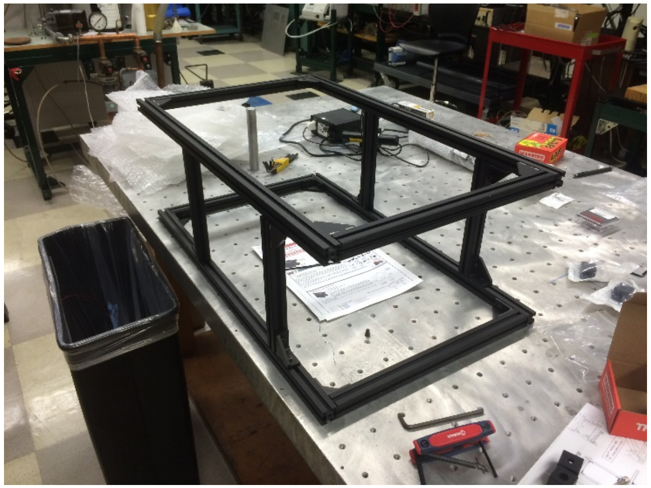


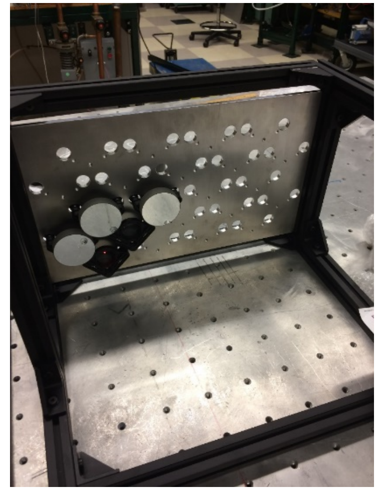


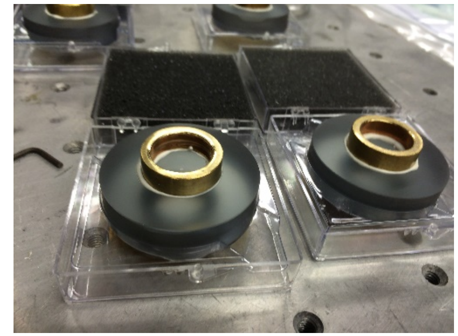


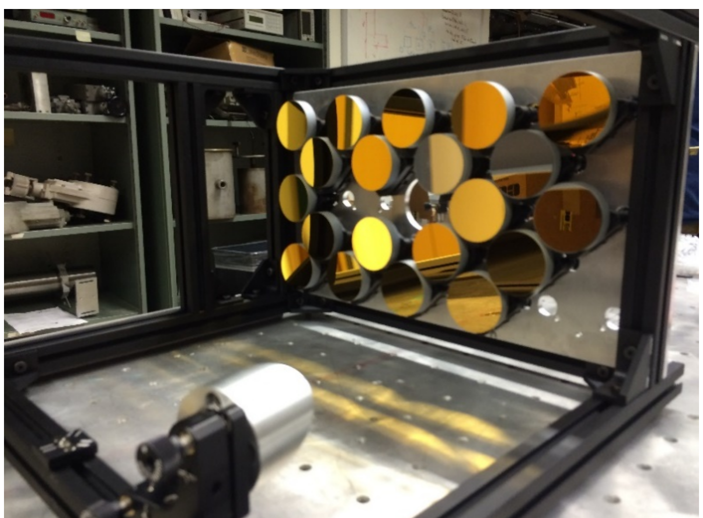


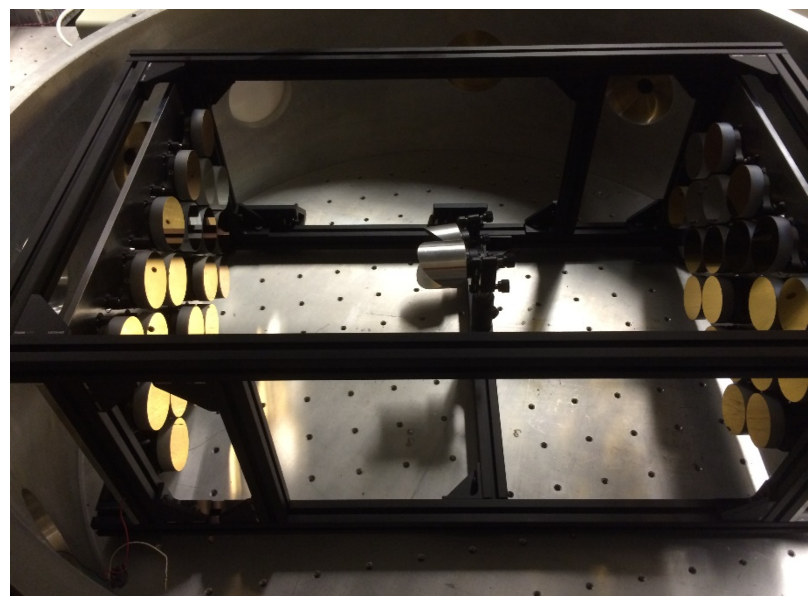
Multipass assembly



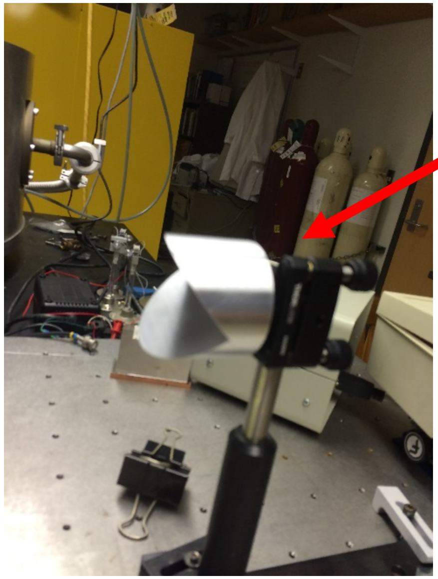








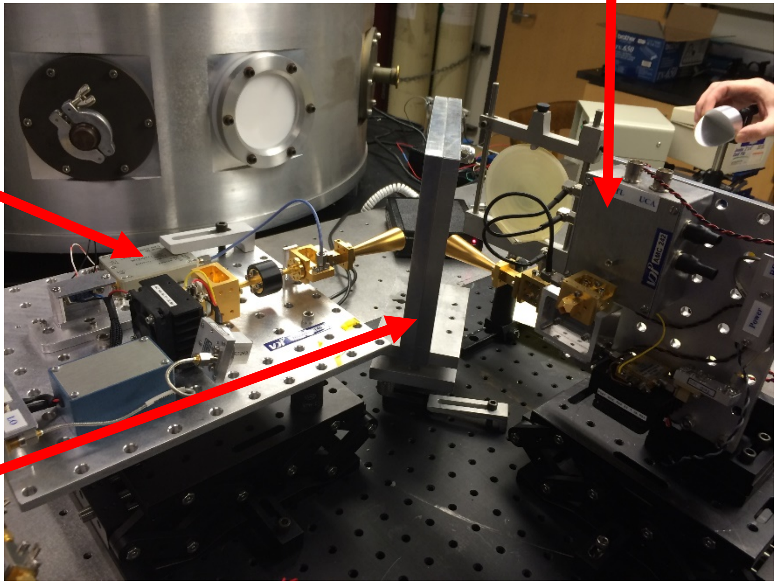
Multipass assembly



Polarization-rotating retroreflector constructed in machine shop

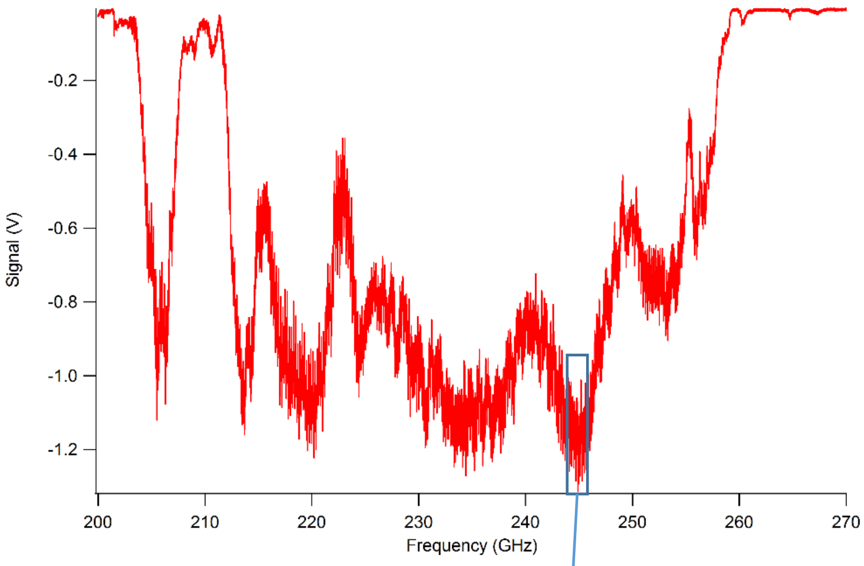
Transmitter

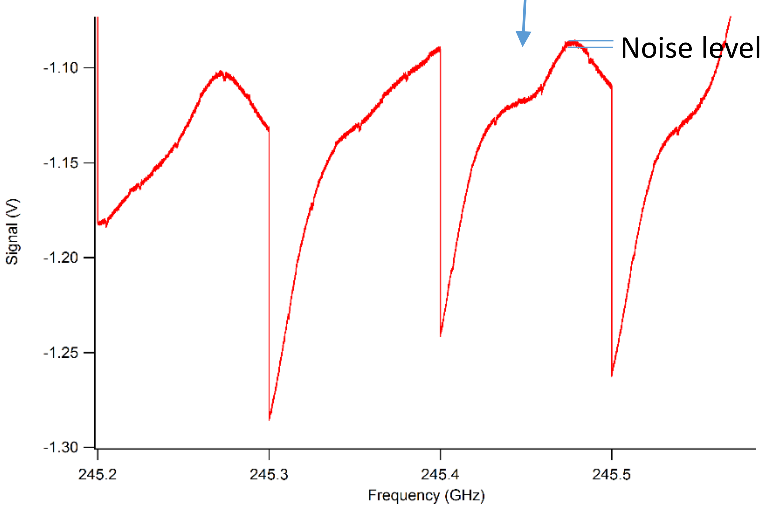
Receiver



Wire grid beamsplitter

Multipass characterization



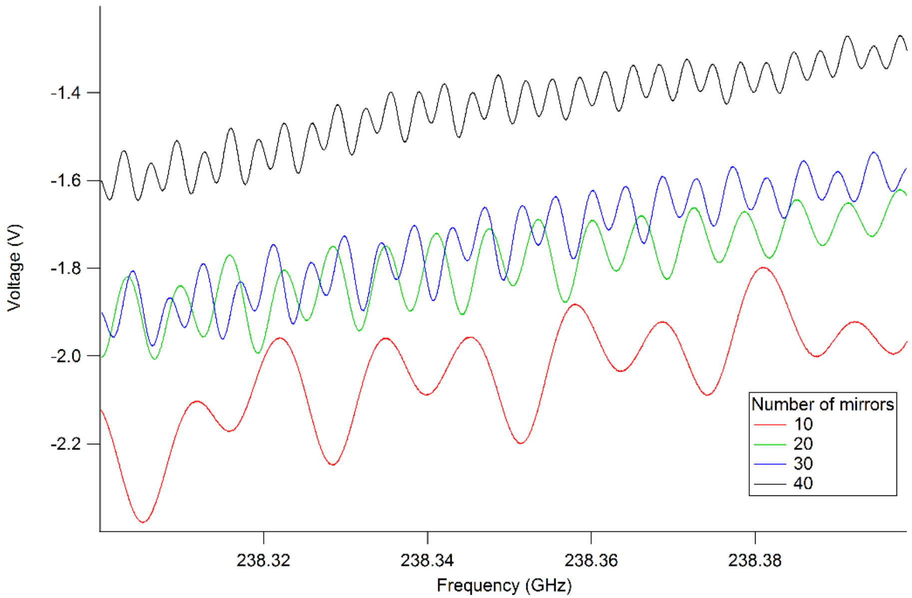


Baseline changes with increasing mirrors

Decreased baseline intensity

Increased baseline fringe frequency

Decreased baseline fringe intensity

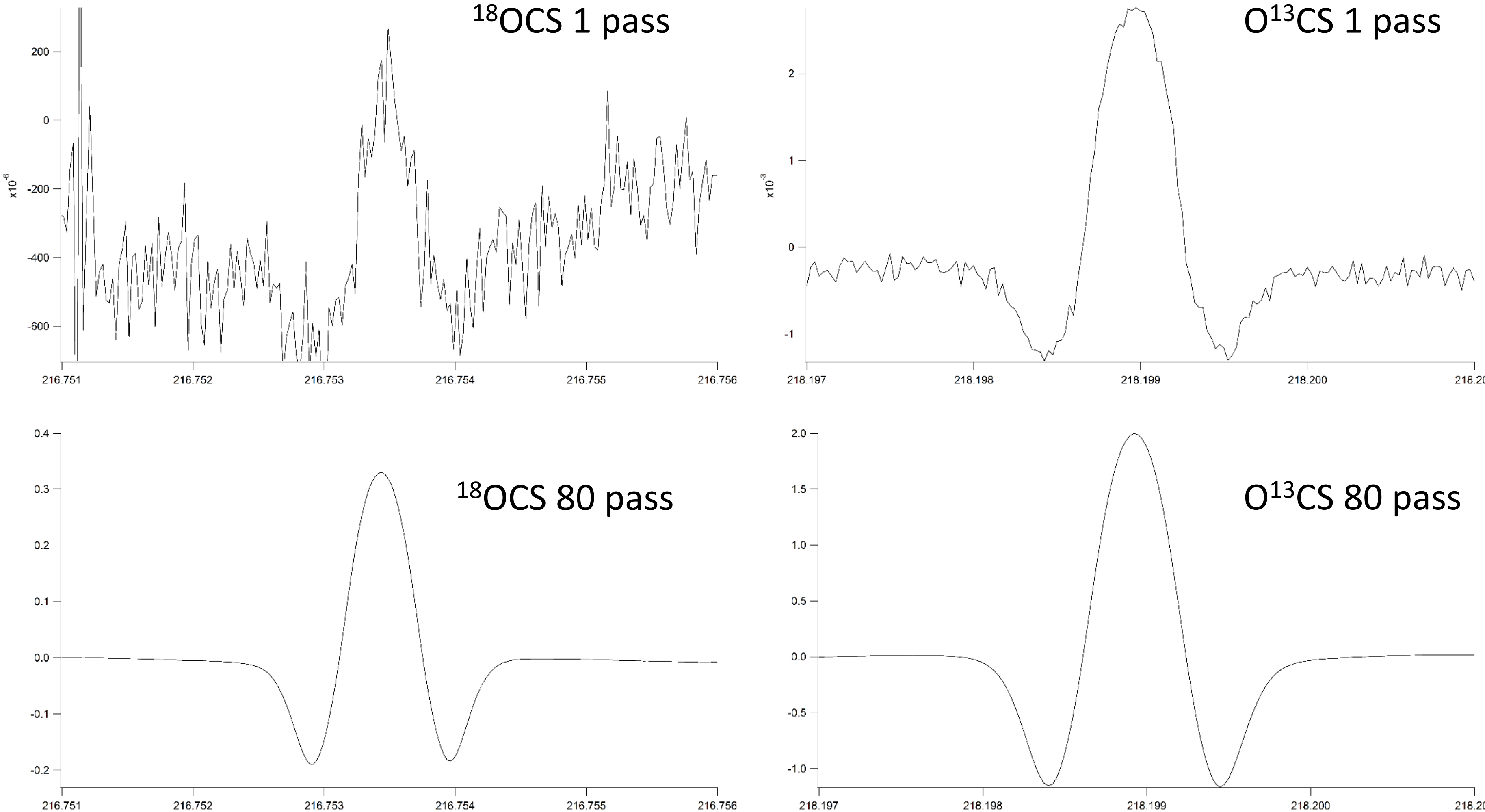


Average reflectivity = 99.3%

Test measurements: Carbonyl sulfide

- Simple linear rotor
- Conduct system diagnostic measurements
- Approx. 5 mTorr neat OCS in multipass cell
- Compare single pass vs. multipass
  - Estimate total gain from multipass
  - Estimate sensitivity, SNR
- Access to multiple isotopomers
  - OCS, $OC^{34}S$ (4%), $O^{13}CS$ (1%), ^{18}OCS (0.2%)

OCS (neat, 5.5 mTorr)

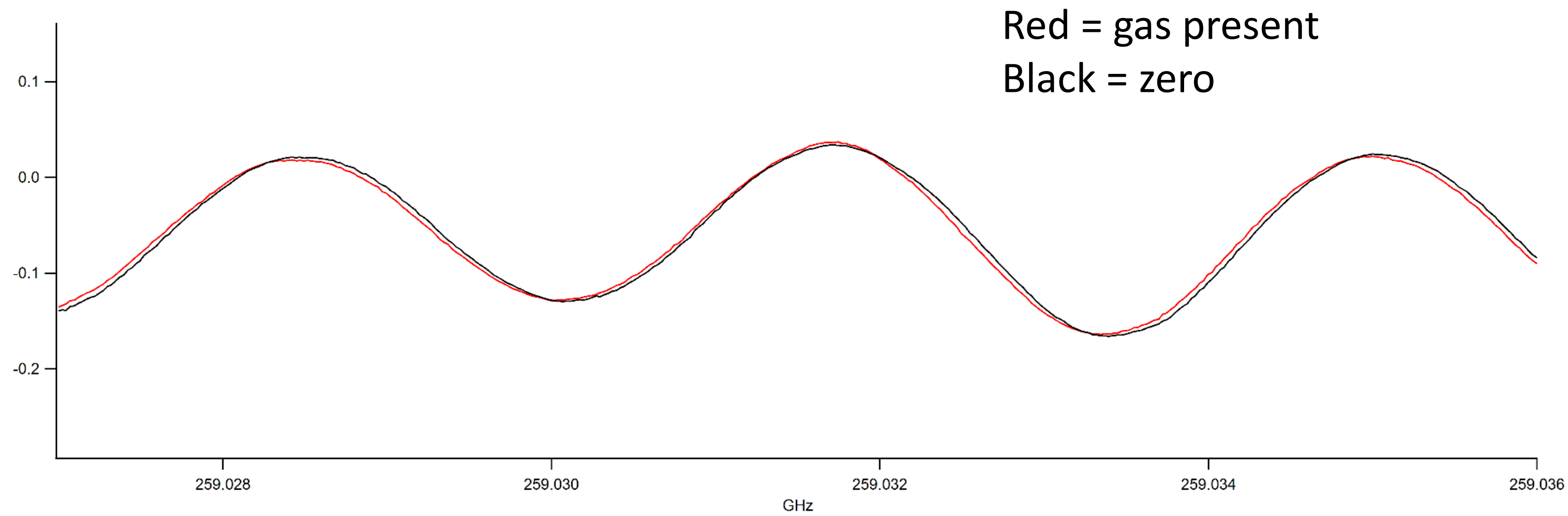


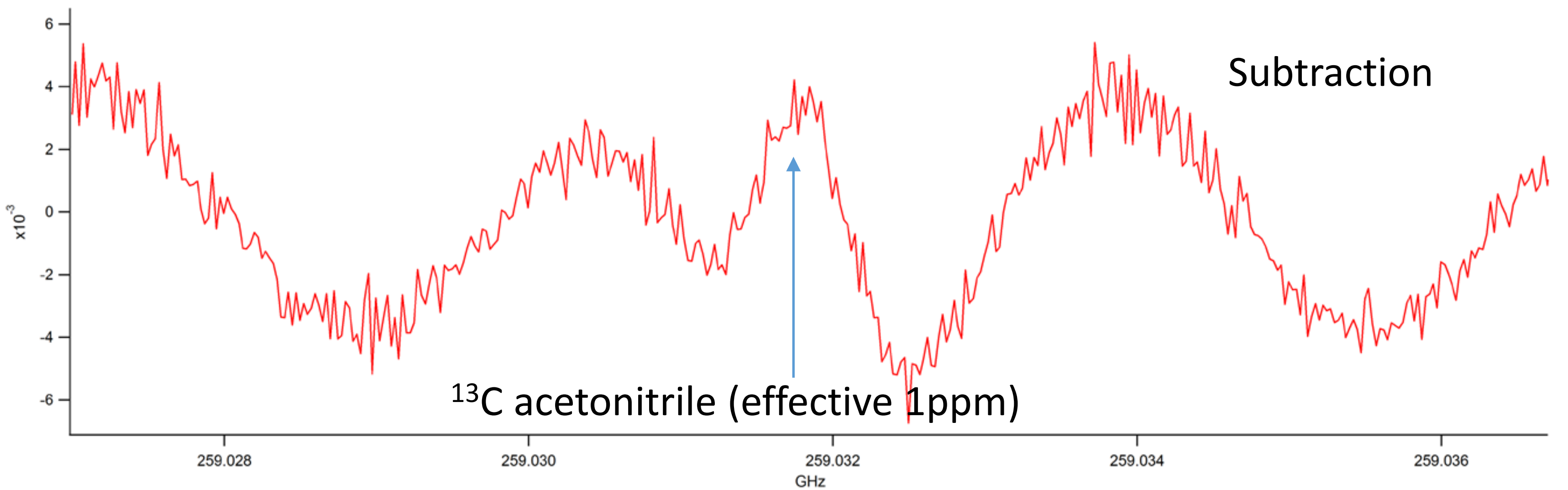
~2,000 ppm ~10,000 ppm

Test measurements: Acetonitrile

- Diagnostic tests at intermediate dilution
- 100 ppm CH_3CN in N_2
- Demonstrate detection of ^{13}C isotopomer (1% of normal species, ~1 ppm)
  - 80 pass configuration only
- Results
  - Detected ^{13}C isotopomer with decent SNR
  - Suggested that 1 ppm H_2CO is feasible

CH_3CN (100 ppm in N_2)

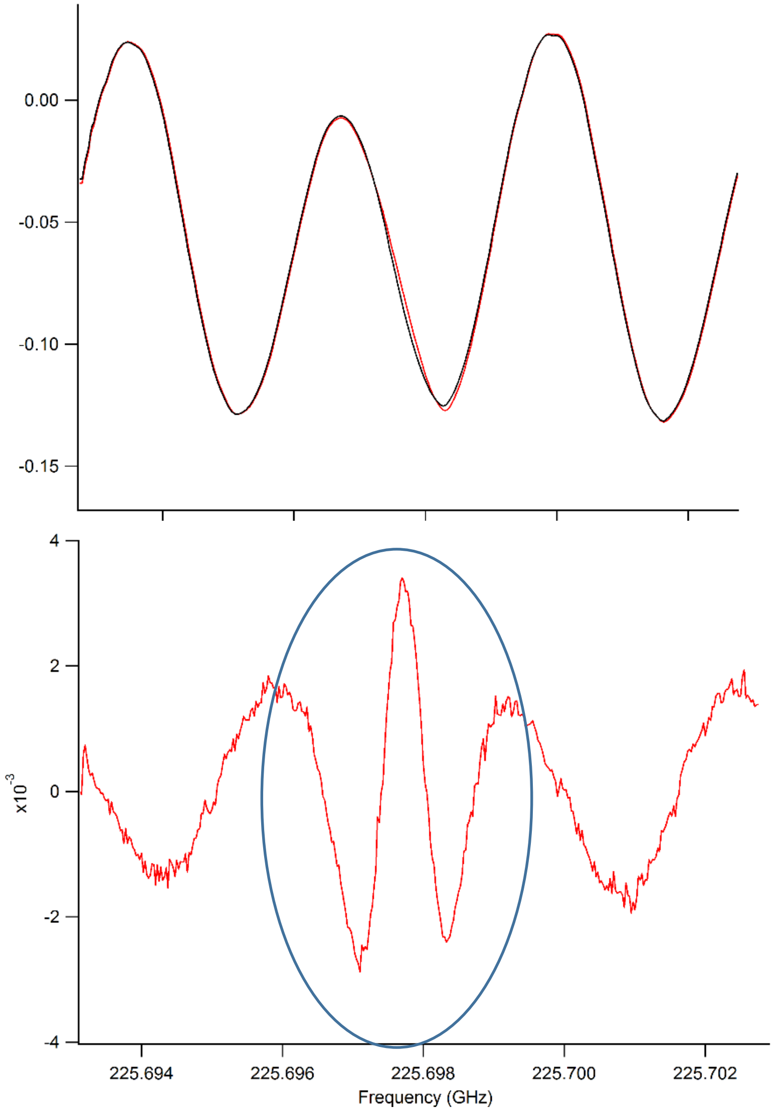




Test measurements: Formaldehyde

- Preliminary sensitivity tests
- Detect 1 ppm H_2CO in N_2
- Results
    - Detected strongest line at 20:1 SNR
    - Equivalent detection of approx. 50 ppb
    - No additional efforts taken to enhance signal or reduce noise

Formaldehyde (1 ppm in N_2)



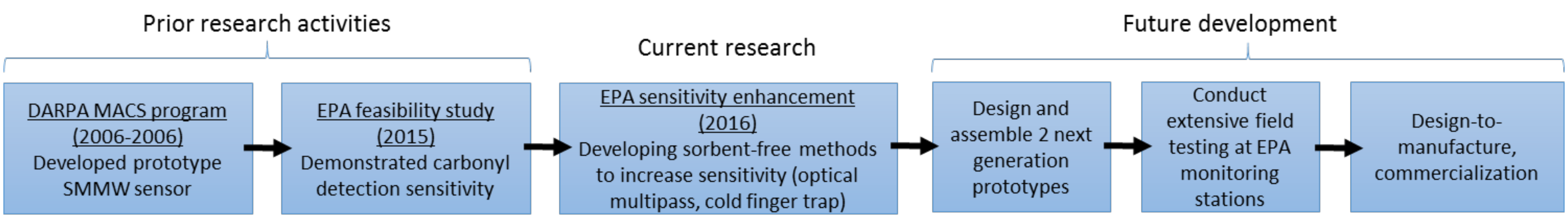
- Baseline fringes x20 intensity of H_2CO line
- Residual baseline fringes on subtracted signature
- SNR ~20
- Additional optimization needed

Next steps

- Sensitivity optimization (ppb-level detection)
  - Compensation for baseline fringes
    - Algorithm approach
    - Leverage astrophysical procedures
  - Increased signal averaging
  - Decreased scan rate
  - Assess SMMW power and saturation effects
- Cold finger preconcentration
  - No consumables

Technology development

- Development of ambient air monitoring prototypes
- Field testing at EPA monitoring stations
- Commercialization



Conclusions

- SMMW spectroscopic sensor enables highly sensitive detection of carbonyls
- Optical multipass shows promise for approaching formaldehyde MDL (0.065 ppb)
- Additional optimization of sensitivity required
- Path to commercialization defined