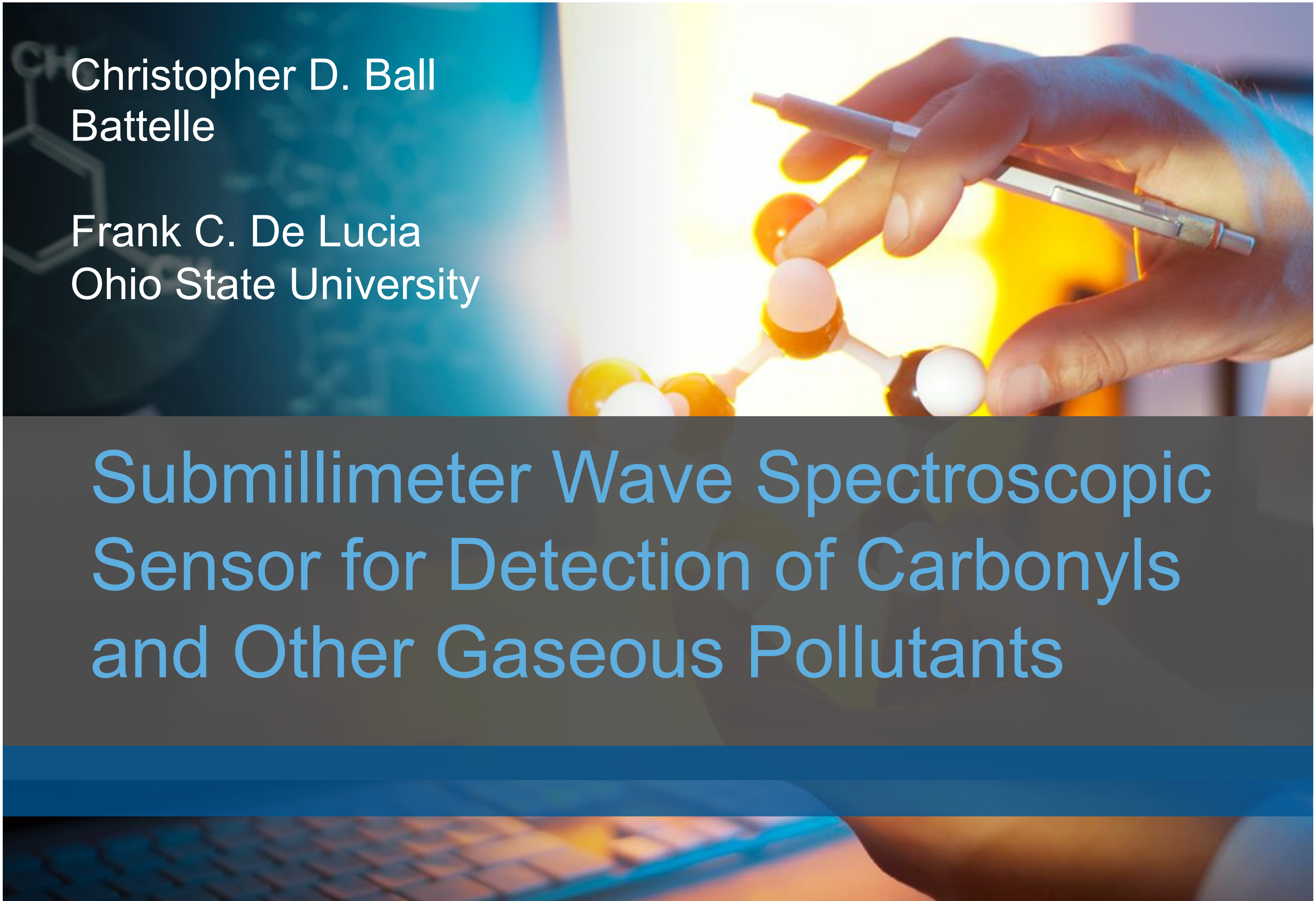

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Submillimeter Wave Spectroscopic Sensor for Detection of Carbonyls and Other Gaseous Pollutants

THE OHIO STATE UNIVERSITY

Battelle
The Business of Innovation

Introduction

- Submillimeter wave (SMMW) spectroscopic gas sensor
  - Developed by Battelle and OSU for DARPA

  - Offers significant gains in sensitivity, selectivity, and speed
- Adaptable to air pollutant monitoring applications
  - Direct detection of formaldehyde, acrolein, NO_2, etc.
  - Simultaneous detection of multiple criteria pollutants
  - Reduced reliance on lab-based sample analysis

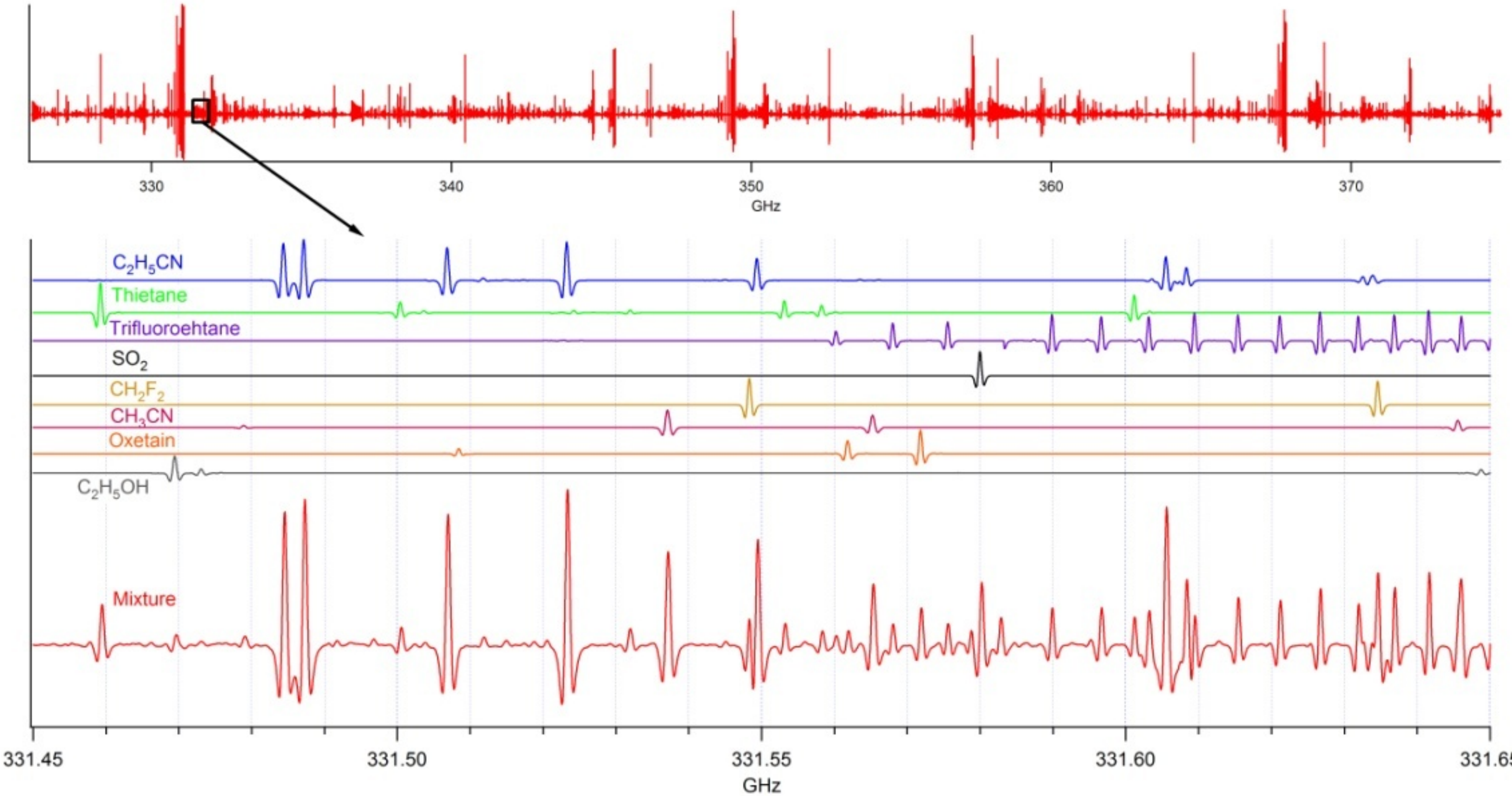
Overview

- Advantages of SMMW spectroscopy
- Development of a SMMW-based sensor
- Relevance to gaseous pollutant detection
- Ability to identify specific chemicals of interest
- Key sensor technology discriminators
- Path forward, technology development roadmap

SMMW Spectroscopy

- High resolution SMMW spectroscopy exploits molecular rotational transitions
- Uniqueness and redundancy of signatures provide near-absolute specificity
  - Optimal pressure ~10 mTorr - Doppler limit
  - Small number of molecules required for detection
- Laboratory SMMW spectroscopy is very mature (50+ years)

Example Spectra



Advantages of SMMW Sensor

- Technology now available for small (1 ft^3) system (100-600 GHz)
- Potential for very high sensitivity (ppt) if incorporate preconcentration
- Very high specificity → Low false alarm rate
- Fast measurement and analysis (sec to min)
- Broad range of target analytes

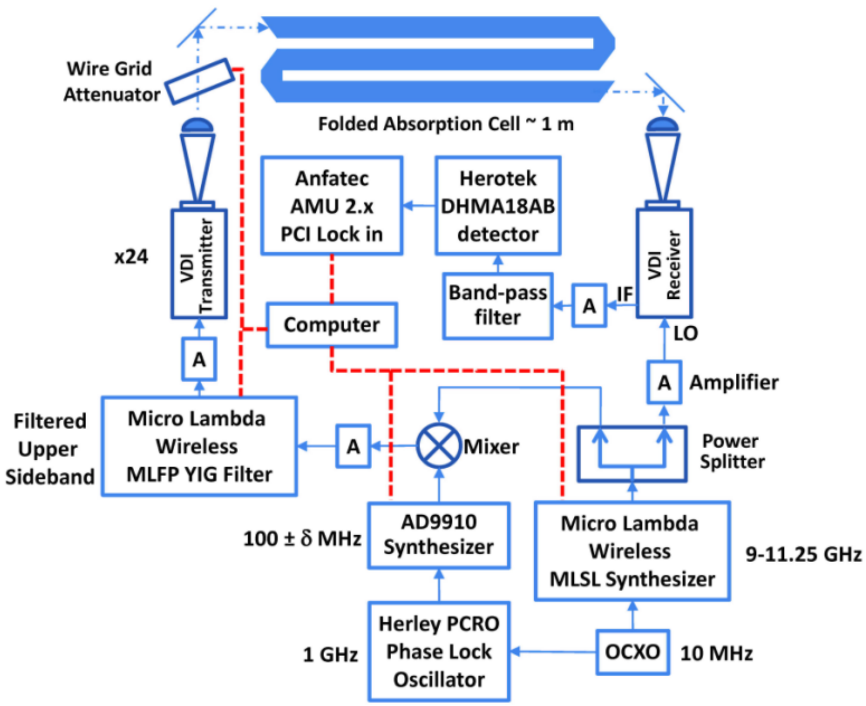
Neese, et al., "Compact Submillimeter/Terahertz Gas Sensor with Efficient Gas Collection, Preconcentration, and ppt Sensitivity," *IEEE Sensors Journal* vol. 12, pp. 2565-2574, 2012

Disadvantages of SMMW Sensor

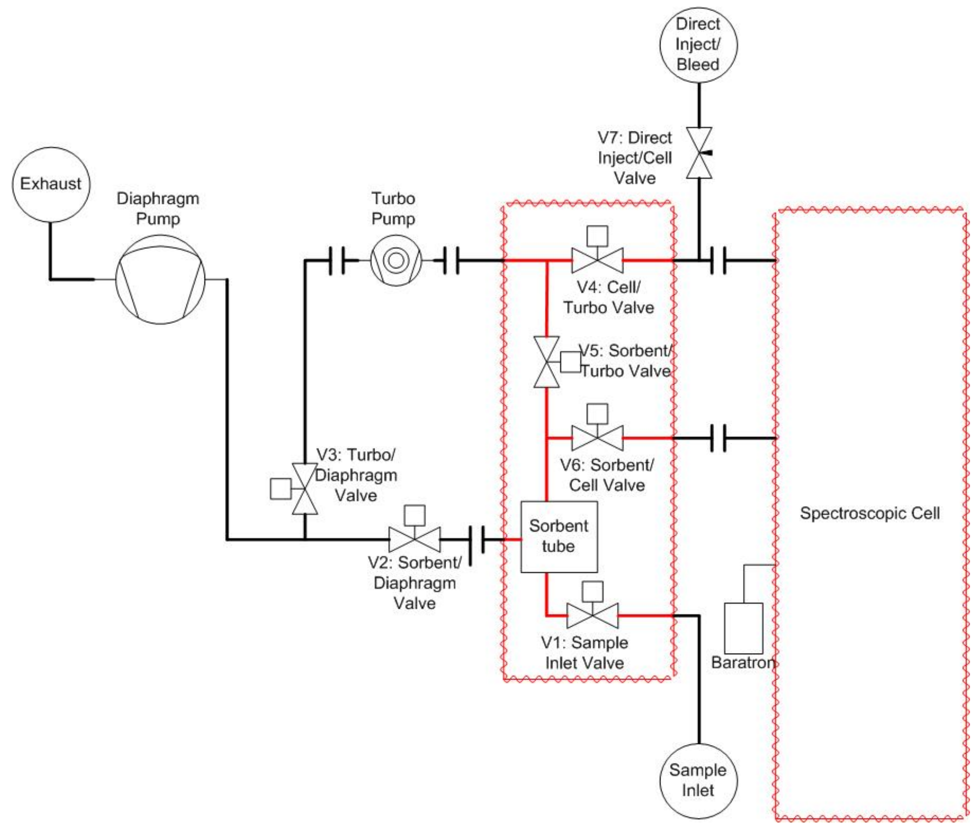
- System cost currently high for pollution monitoring applications (> $100k)
  - Continued tech development will drive down cost
- Dipole moment required
- Difficult to detect large/complex molecules
  - Additional research required to incorporate alternative techniques
- Some smaller molecules (NH_3, HF, etc.) require high frequency sources (600 GHz)

SMMW Sensor Design

Spectrometer

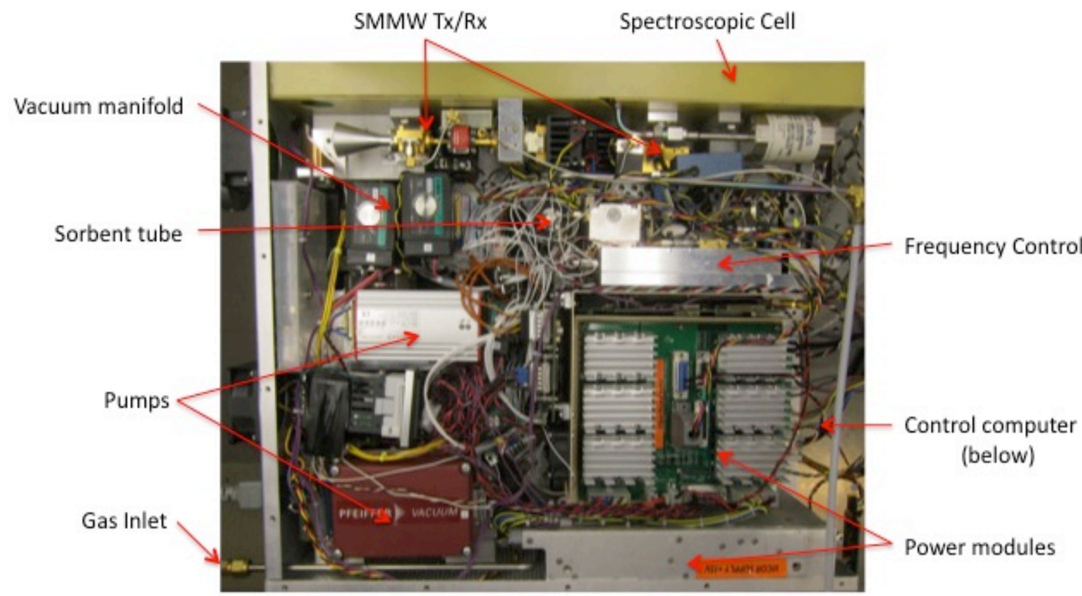


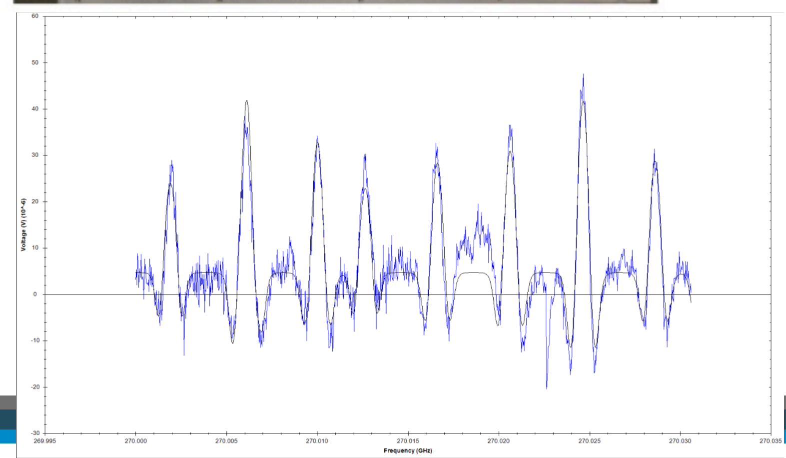
Sample Handling



DARPA Mission Adaptable Chemical Sensor (MACS) Program

- Met or exceeded all DARPA metrics
  - Sensitivity: ~ppt
  - Selectivity: simultaneous detection of 30+ gases
  - False alarm rate: < 10^{-10}
  - Speed: 10 min
  - Size: 1 cubic foot



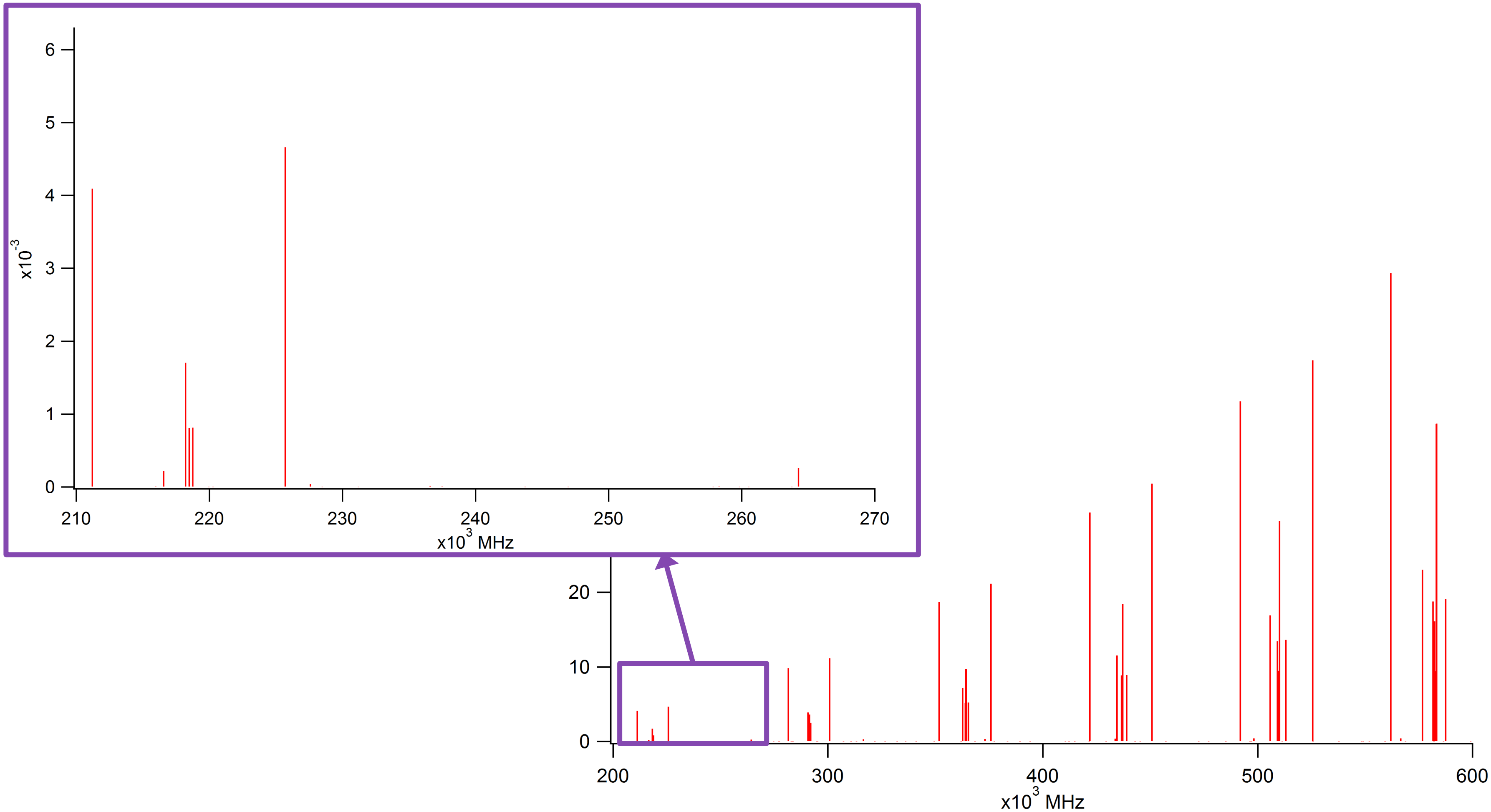


Detection of Gaseous Pollutants

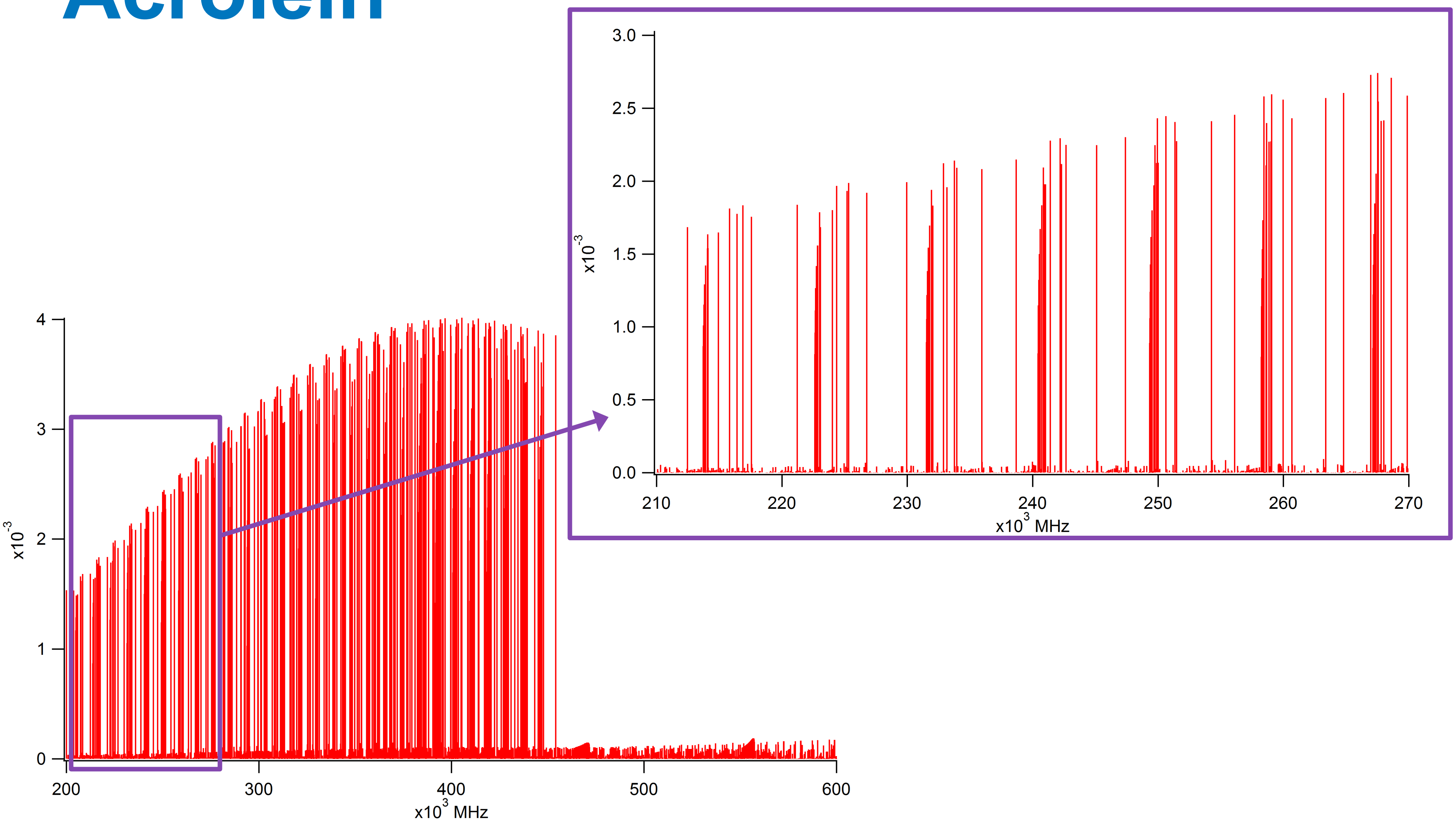
- Ability to detect carbonyls, NOx, SOx, etc.
  - New EPA-funded task (contract EP-D-13-005) to assess carbonyl detection feasibility
  - Effort led by OAQPS (Dave Shelow), emphasis on formaldehyde, acrolein, and acetaldehyde
- Simultaneous detection of multiple pollutants
- Sufficient sensitivity for air monitoring (ppb-ppt)
- Near real-time monitoring capability
- Maturation of technology expected to enable development of ~$20k system

Formaldehyde

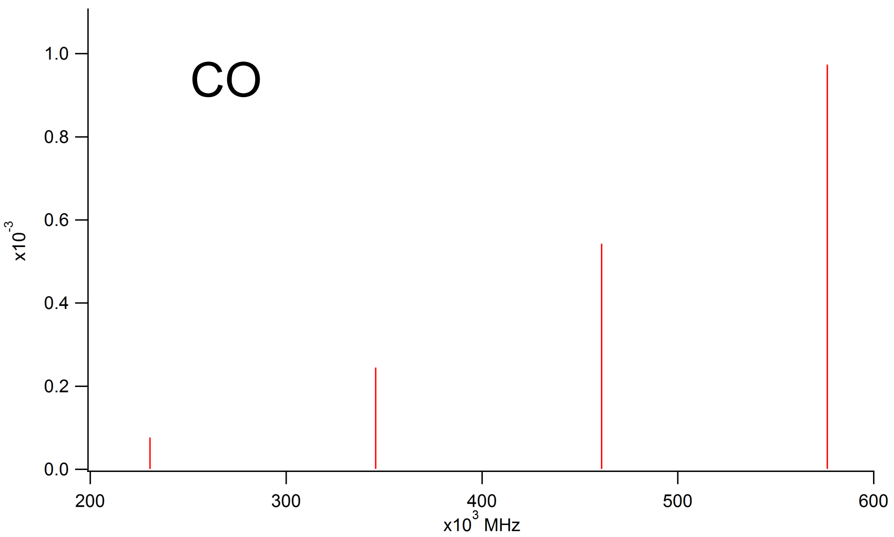
Spectral data from NASA JPL catalog:
http://spec.jpl.nasa.gov/



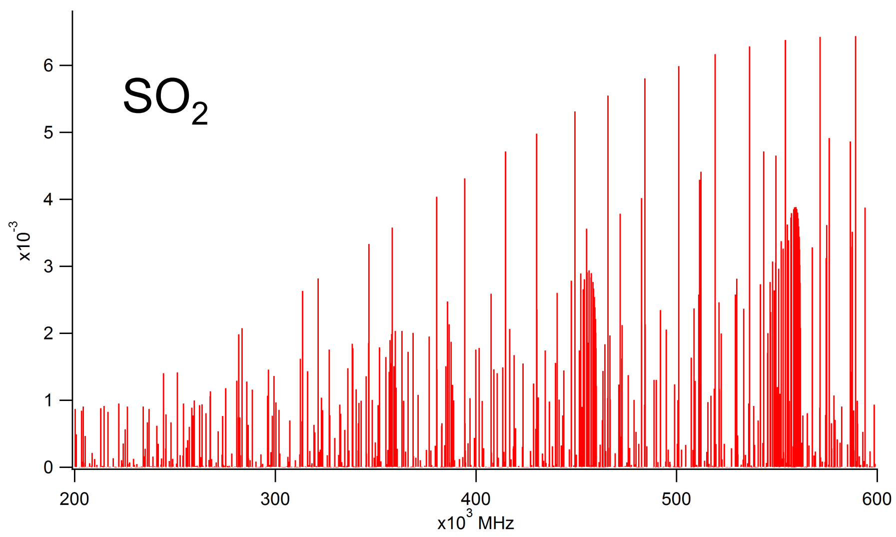
Acrolein


3.0
2.5
2.0
1.5
1.0
0.5
0.0
x10-3
210
220
230
240
250
260
270
x10³ MHz
4
3
2
1
0
x10-3
200
300
400
500
600
x10³ MHz

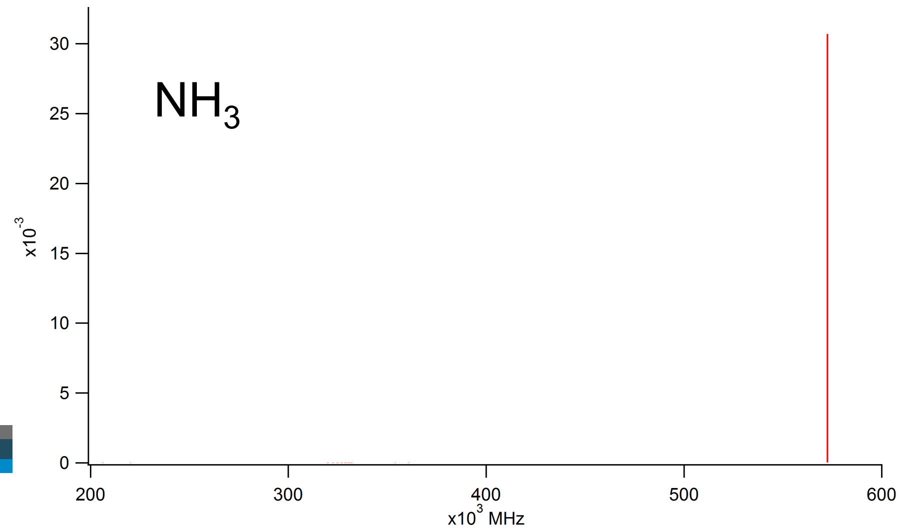
CO, SO_2, NH_3



CO
1.0
0.8
0.6
0.4
0.2
0.0
x10-3
200
300
400
500
600
x10^3 MHz

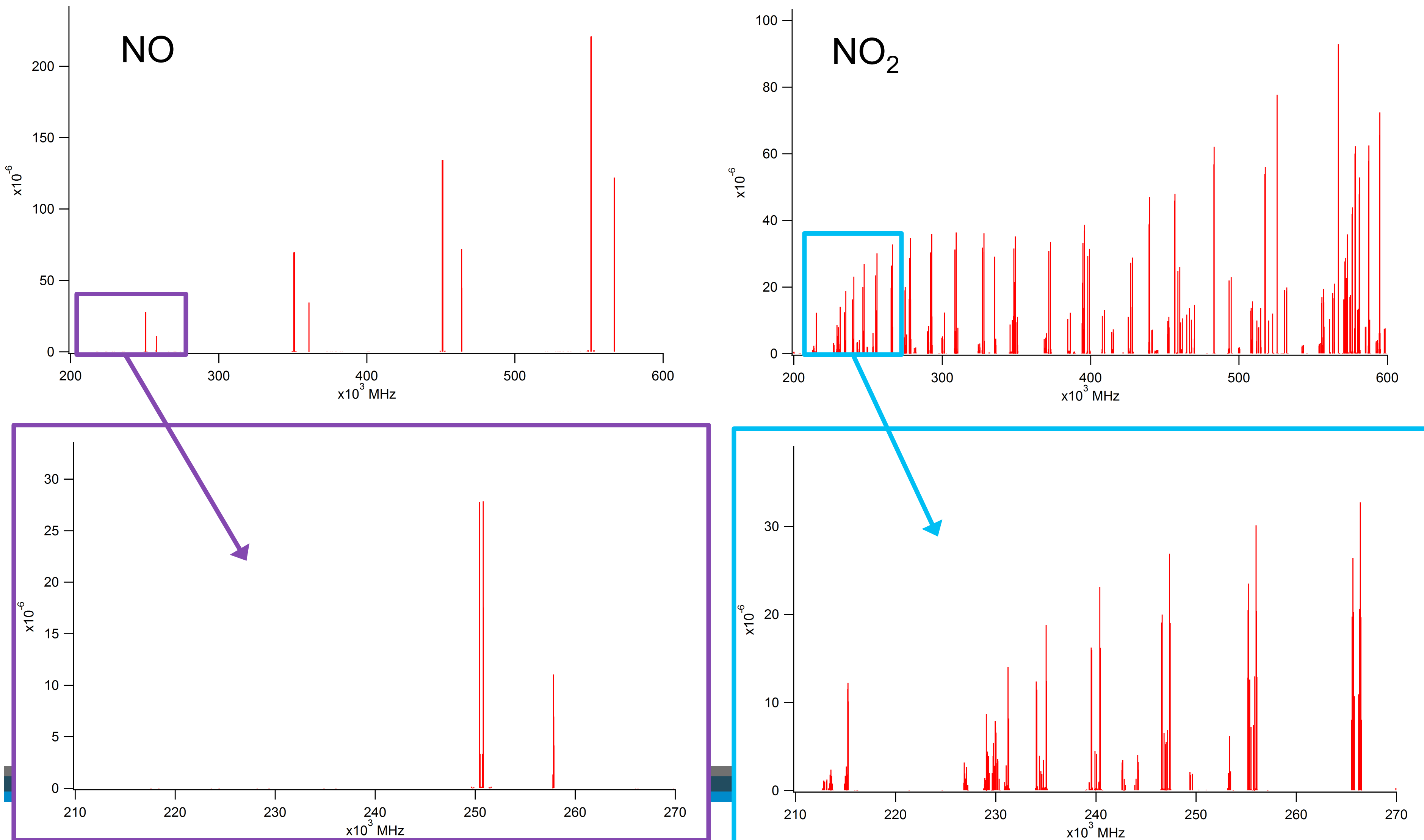


SO2
6
5
4
3
2
1
0
x10-3
200
300
400
500
600
x10^3 MHz

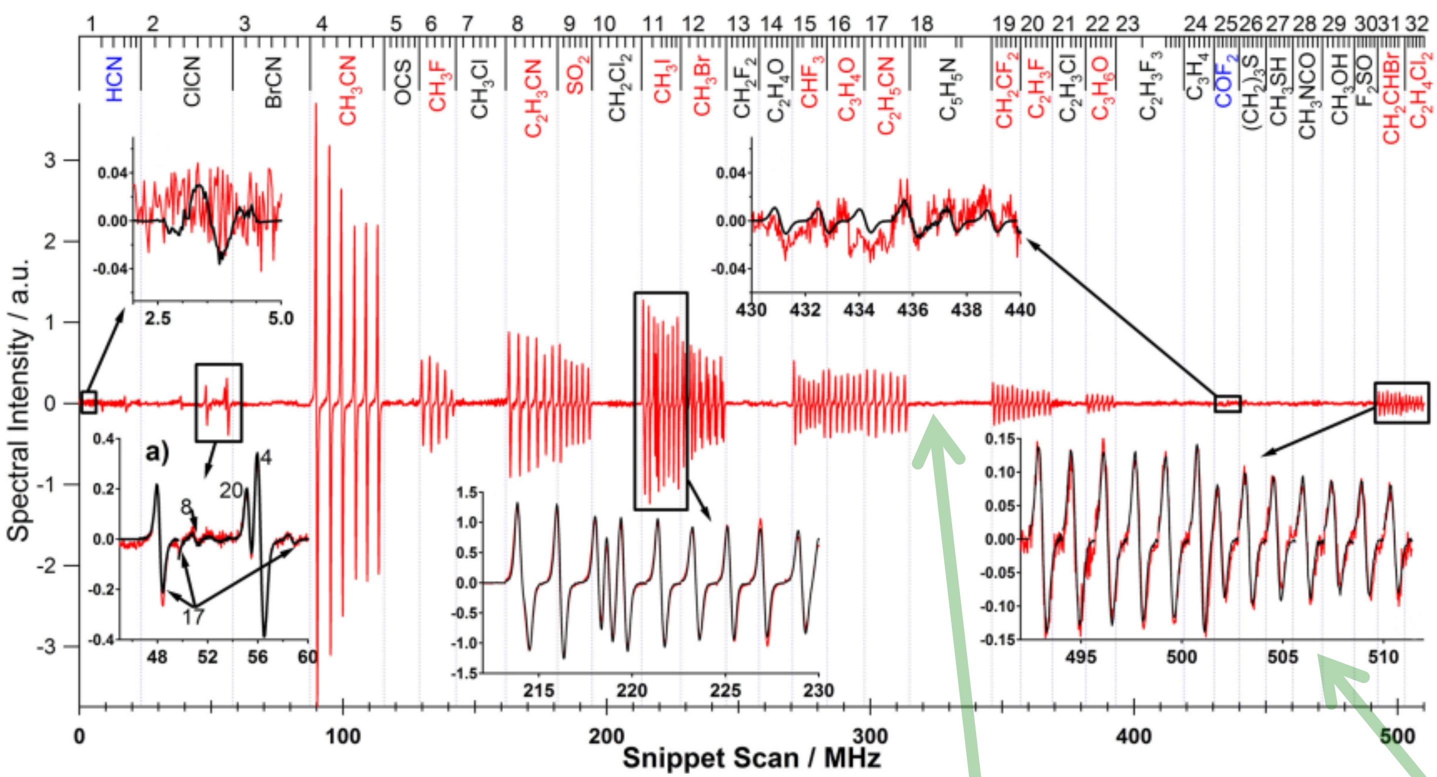


NH3
30
25
20
15
10
5
0
x10-3
200
300
400
500
600
x10^3 MHz

NO and NO_2



Simultaneous Detection



	Pressure /μtorr	S/N
1	0.06	5.0
2	0.00	0.4
3	0.02	1.3
4	61.79	598.2
5	-0.02	0.5
6	26.97	304.7
7	0.00	0.1
8	66.09	432.5
9	54.13	323.8
10	0.12	1.2
11	130.10	404.2
12	85.04	390.4
13	0.16	1.0
14	-0.02	0.1
15	70.05	273.0
16	58.93	281.2
17	60.61	321.7
18	-0.12	0.8
19	55.67	192.8
20	40.31	161.3
21	-0.55	2.0
22	30.09	92.8
23	-0.07	0.3
24	-0.16	0.5
25	4.68	9.5
26	-0.90	1.8
27	0.10	0.2
28	0.81	1.5
29	0.27	0.6
30	-0.63	1.1
31	71.78	123.2
32	73.12	82.6

Σ = 0.89 mtorr

System scans six (selectable) snippets for each of 32 (selectable) chemicals

Compares the resultant spectra with an intensity calibrated library

Does LSQ to determine concentrations

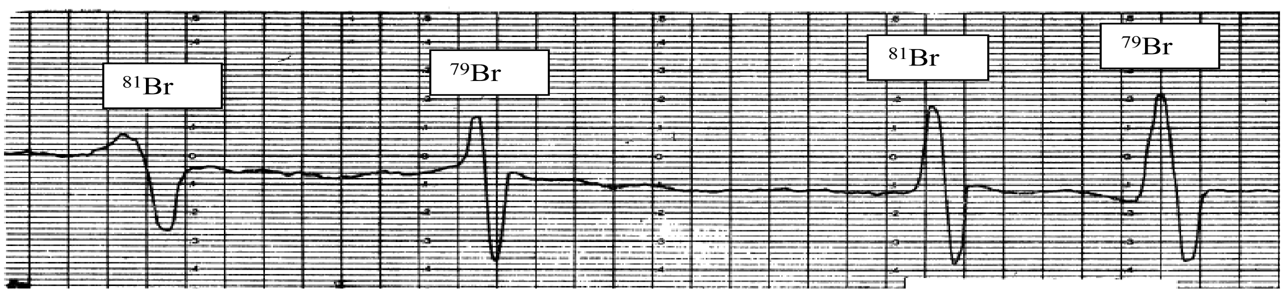
Intensity calibration is fundamental for analysis

Sensitivity Considerations

- Very small amount of sample needed
  - Femtomole detection possible
  - IR systems of similar ppx sensitivity need 4 OM more sample
- Additional sensitivity by increasing:
  - Sample acquisition (more molecules), signal integration (enhanced S/N), cell length (absorption ~ path length)
- Dynamic range
  - Non-linear effects occur when "too much" sample is present
  - Can adjust via algorithm or bypass sorbent

Specificity Advantage

- High specificity based on narrow rotational spectral signatures
  - Pd ~ 0.9999, Pfa << 10^{-10}, simultaneous 30+ gases detect
- Rotational lines provide unique “fingerprint” without complicated processing or data analysis
- High specificity enables accurate isotope detection



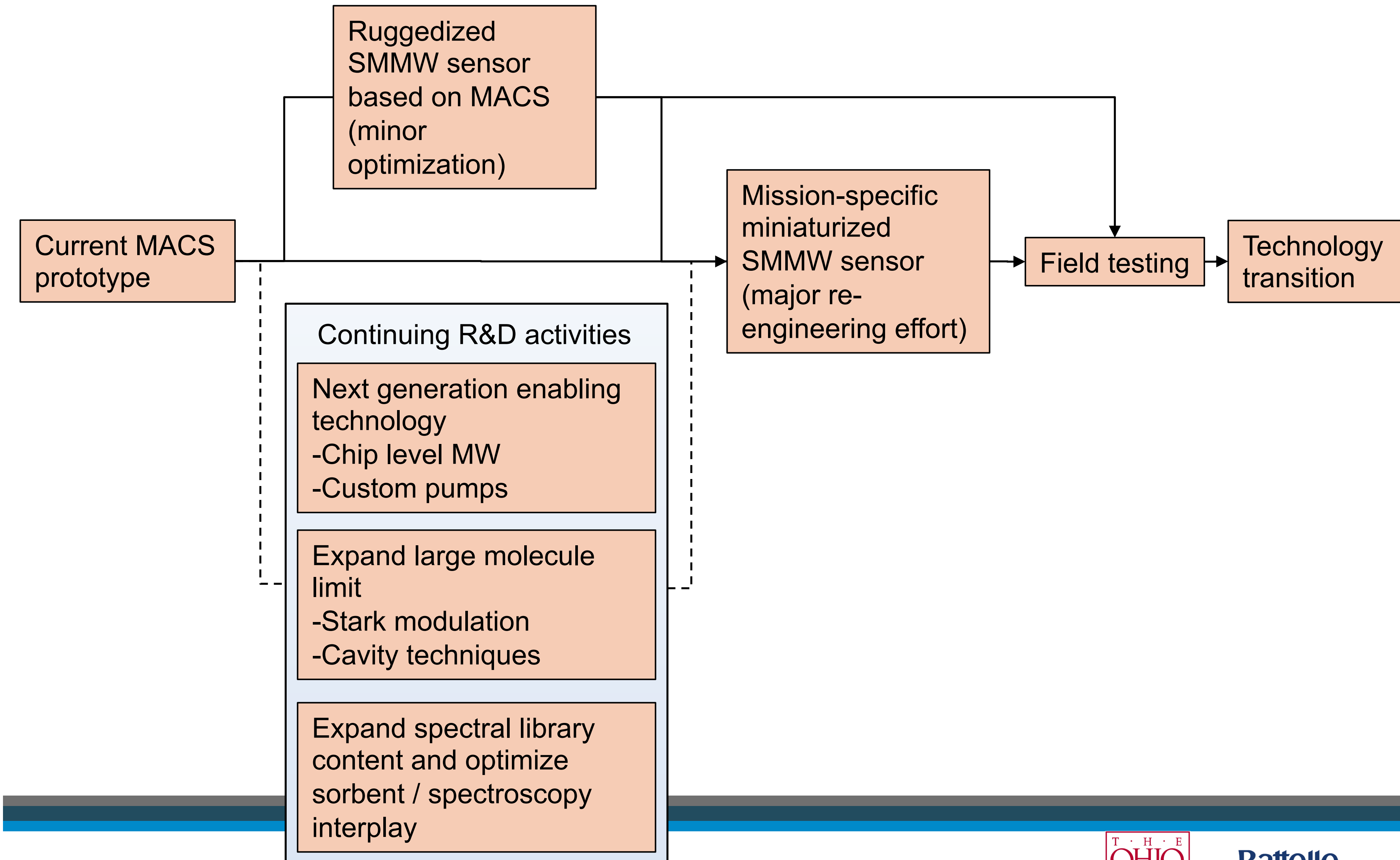
Environmental Factors

- Sensor not currently ruggedized for outdoor use
- Filter on gas sample inlet prevents dust and other particulates from entering sorbent preconcentrator
- Temperature variations negated using temperature controlled cell, held slightly above ambient
- Sensor is immune to some background effects such as humidity or common pollutants
  - Key detectable interferents can be discriminated
  - Humidity may cause sample dilution, but not interference

SMMW Technology R&D

- Spectrometer cost reduction and miniaturization
  - Current MACS technology uses robust commercial MMW multipliers and amplifiers that cost ~$70K
  - Advances in wireless communications technology moving toward chip-level devices that can produce 100 GHz and cost ~$100
  - Leveraging advances in CMOS technology funded by Semiconductor Research Corp
  - Following advancements at IBM to extend current Tx/Rx of 60 GHz to ~240 GHz

Sensor Development Roadmap



Conclusion

- SMMW sensor provides flexibility to detect multiple air pollutants simultaneously in near real-time
- Concept proven by meeting performance metrics on DARPA MACS program
- Development of ruggedized, autonomous, inexpensive sensor is feasible
- Can broaden scope of air monitoring, fill gaps in continuous monitoring of formaldehyde and acrolein, offer direct NO_2 detection, and reduce lab-based sample analysis costs

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