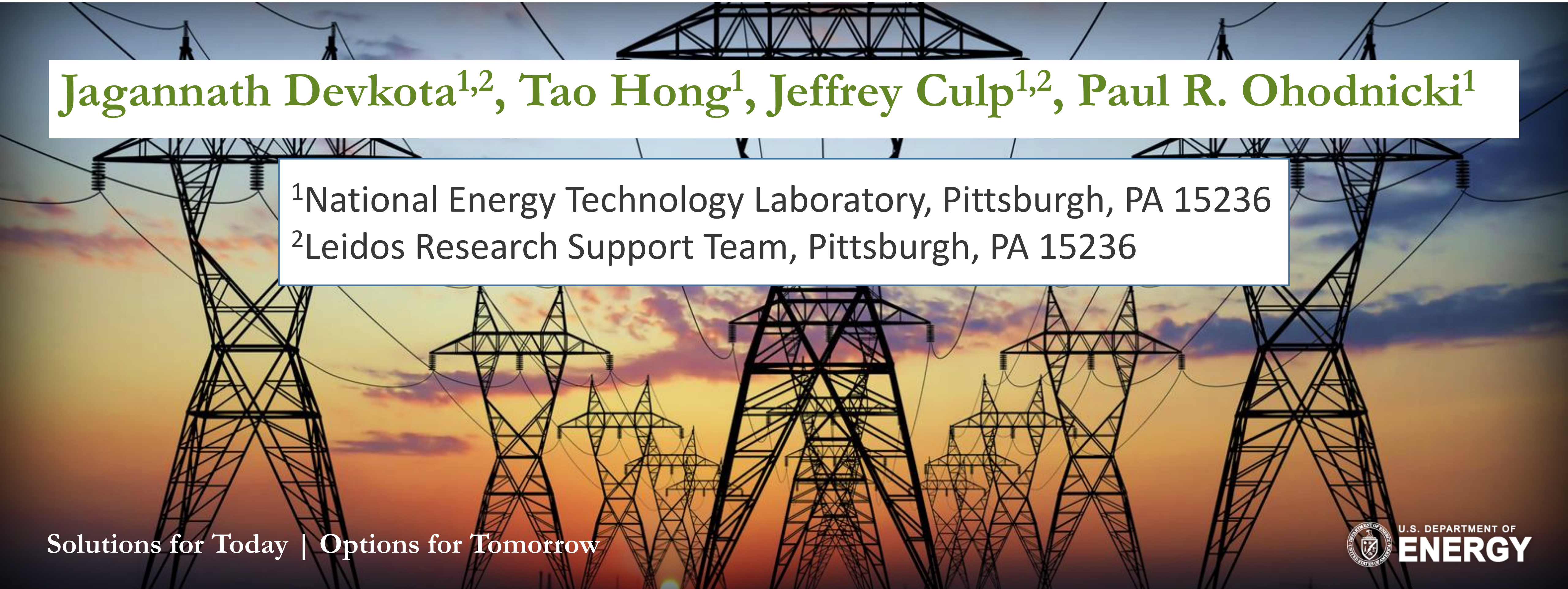
Development of a wireless surface acoustic wave methane sensor using an MOF as a sensing layer for natural gas pipelines

NATIONAL ENERGY TECHNOLOGY LABORATORY

235th ECS 2019, Dallas, TX, May 26 - 30



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Solutions for Today | Options for Tomorrow

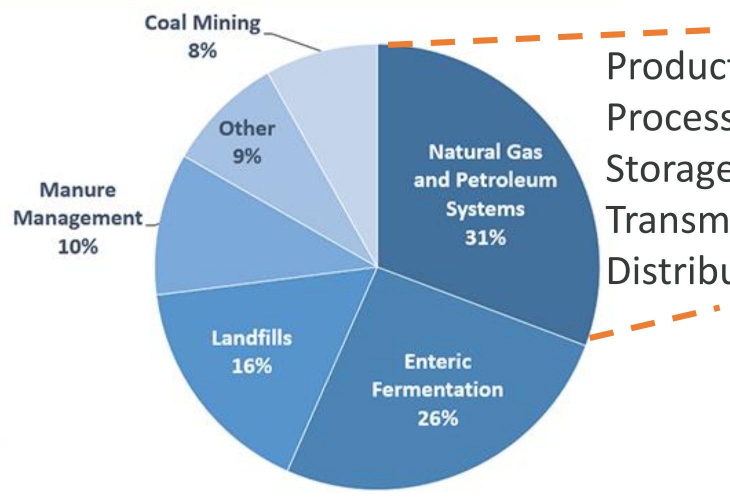
U.S. DEPARTMENT OF ENERGY

Outline

- **Introduction**
  - Methane emissions and consequences
  - Sensors for energy infrastructure monitoring
- **Surface Acoustic Wave Sensors**
  - Working principle
  - Novel sensing materials: Metal-Organic Frameworks (MOFs)
- **Methane Detection**
  - Sensors with ZIF-8 sensing layer
  - Wireless Detection
- **Summary**

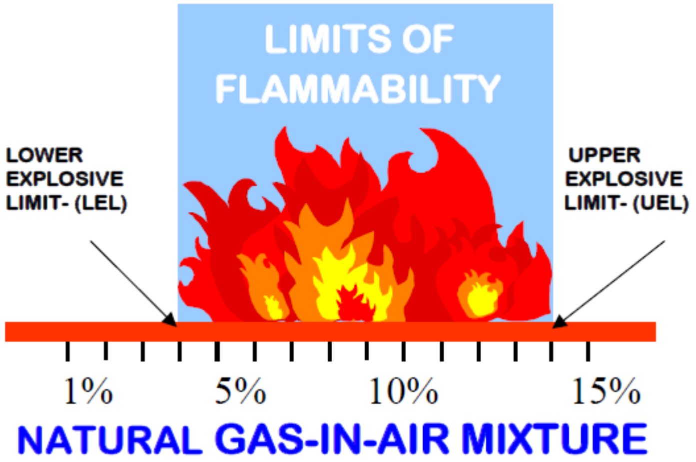
Methane Emissions and Consequences

2016 U.S. Methane Emissions, By Source



Production
Processing
Storage
Transmission
Distribution

U.S. Environmental Protection Agency (2018). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2016



https://www.rrc.state.tx.us/media/8553/chap4-leakdetection-natgas.pdf

Pipeline Explosion Caused by Corrosion

- Environmental Concerns
- Potential Explosions (Leaked Methane Ignition)
- Challenges in Fuel Transportation (Fuel Loss and Maintenance Cost)

How accurate are the current estimates?

"*Methane emission from natural gas system in U.S. and Canada is greater than official estimates*."
(Brandt et. al., Science, 343, (2014), 733)

Opportunity for developing robust detectors for effective monitoring of energy infrastructures and emission sites.

Suite of Complementary Sensing Technologies

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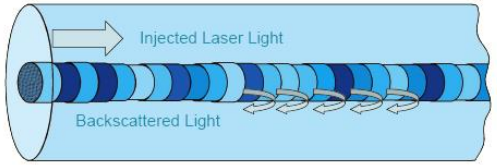
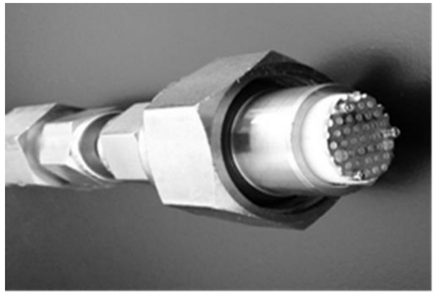
Distributed Optical Fiber Sensors

Imperfections in fiber lead to Rayleigh backscatter:

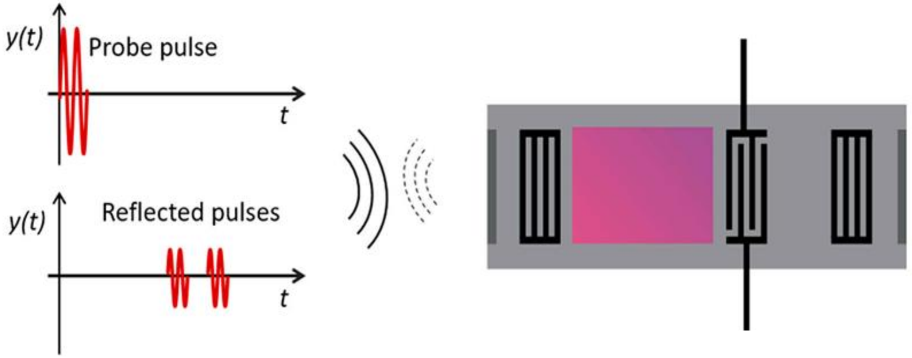


Rayleigh backscatter forms a permanent spatial “fingerprint” along the length of the fiber.

Advanced Electrochemical Sensors



Passive Wireless Sensors



	Geospatial Attributes	Cost	Targeted Function	TRL
Distributed Optical Fiber Sensors	Linear Sensor Adjustable Distance and Resolution	Cost Per Sensor “Node” Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, etc.) Early Corrosion Detection	2-3
Passive Wireless Sensors	Point Sensor	Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, etc.) Early Corrosion Detection	2-3
Advanced Electrochemical Sensors	Point Sensor	Moderate to High	Humidity and Corrosion Rate Monitoring	3-4

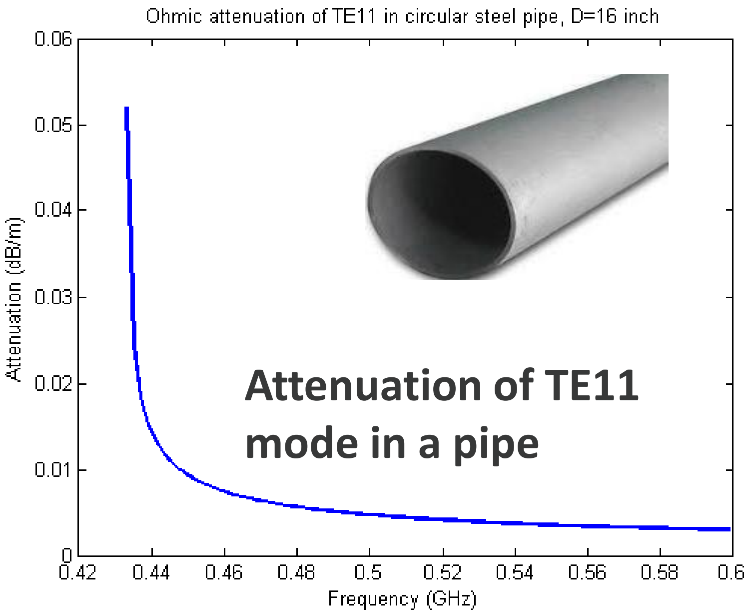
Three Synergistic Sensor Platforms with Complementary Cost, Performance, and Geospatial Characteristics are Being Developed with an Emphasis on Corrosion & Gas Composition.

RF and Microwave Technique for Pipelines

Common pipe sizes for fossil fuel infrastructure

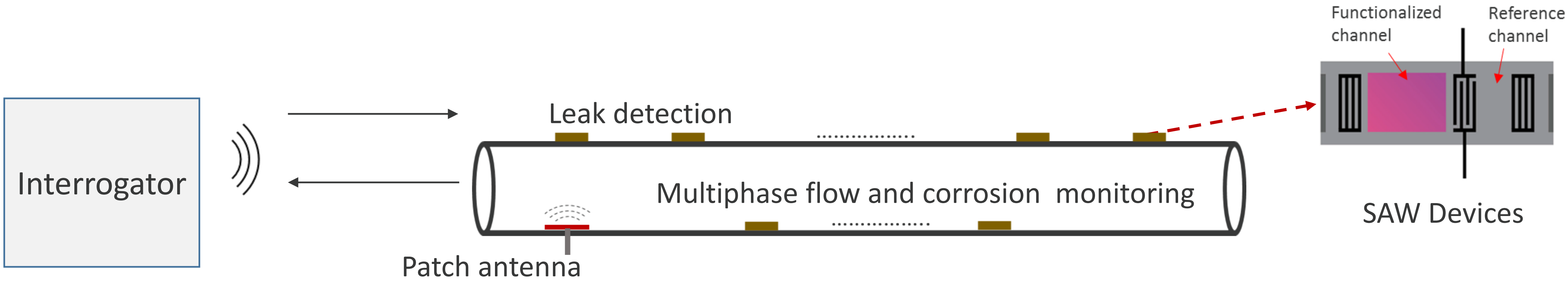
Pipe Type	Diameter (inch)	TE11 Cut off Freq (MHz)
Mainline	16 – 48	433 – 144
Interstate	24, 36	288, 192
Lateral	6 – 16	1153 – 432
Wellbore casing	~4.5	1537
Wellbore tubing	~2.5	2767

16 inch steel pipe:



Loss of ~500 MHz RF Wave in 1km propagation path:

- Free space (isotropic antennas) = 86.42 dB
- TE11 mode conductivity loss (steel pipe) = 10 dB



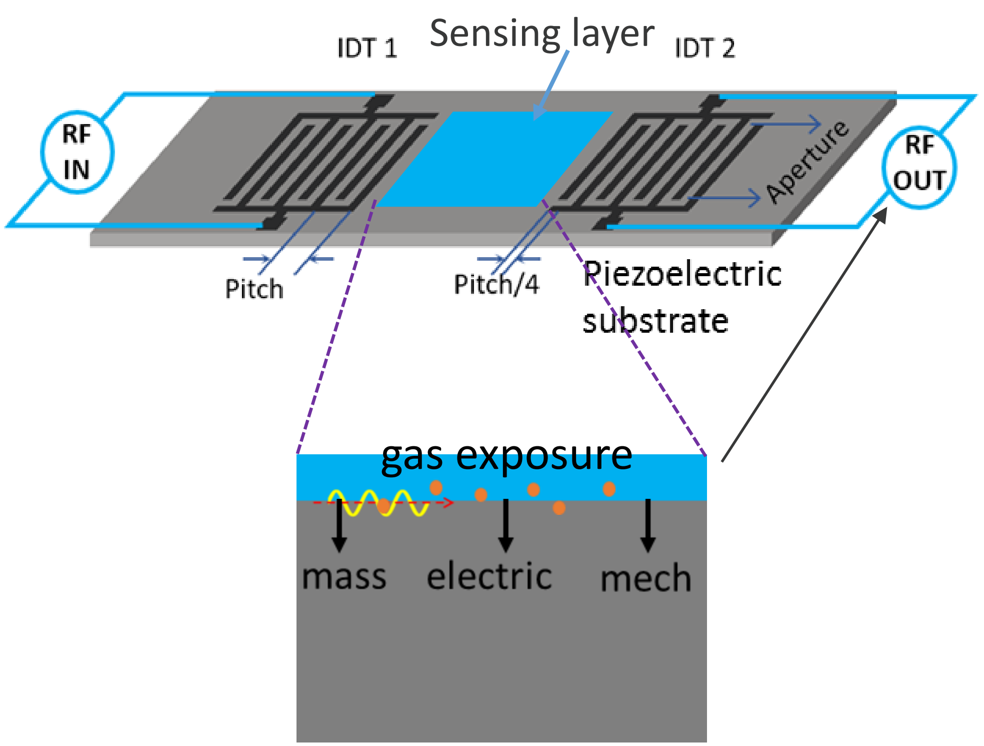
Surface Acoustic Wave Sensors

- Passive, Wireless Sensors Requiring No Active Power (Harsh Environment Compatible, Reduced Maintenance)
- Possible to Develop for Multi-Function Parameter Operation (Temperature, Multicomponent Gas Phase Chemistry)
- Matured Technique: Millions of SAW Filters Produced for Use in Mobile Phones & Commercialized for Temperature Sensing.
- Generally, a **material sensitive to the targeted chemical species** is applied on the transducer surface.

SAW velocity can be recorded in terms of frequency or phase and correlated with a parameter of interest.

$$\frac{\Delta v}{v_0} = \Delta_{temp} + \Delta_{pressure} + \Delta_{mass} + \Delta_{conductivity} + \Delta_{mech} + \ldots\ldots$$

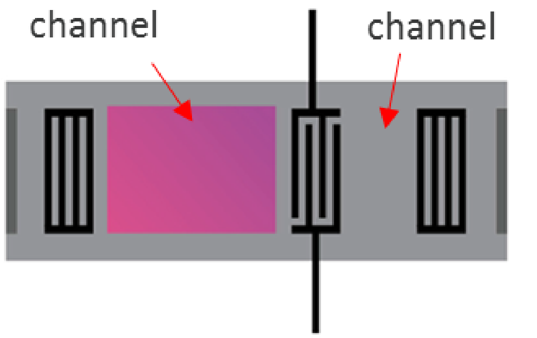
$$\frac{\Delta v}{v_0} = \frac{\Delta f}{f_0} = -\frac{\Delta \phi}{\phi_0}$$



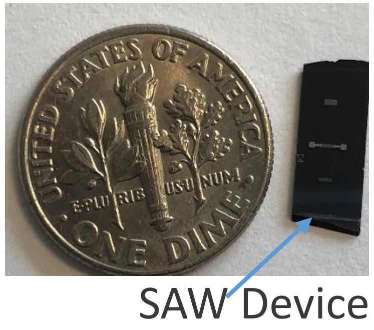
Working principle of SAW gas sensors.

NETL Devices and Experimental Facility

NETL SAW Device Schematic

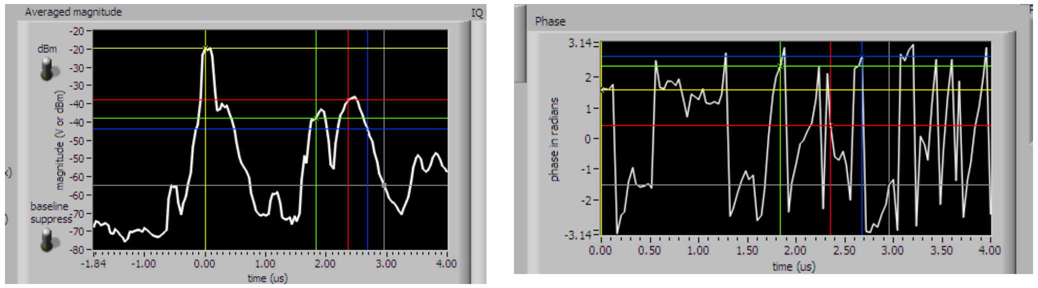


Fabricated Devices



Custom Assembled SAW Interrogator

VNA to Characterize SAWs and Antennas



Real Time Sensors Possible Based on Attenuation or Time Delay

Materials for Methane and In-Pipe Gas Sensing

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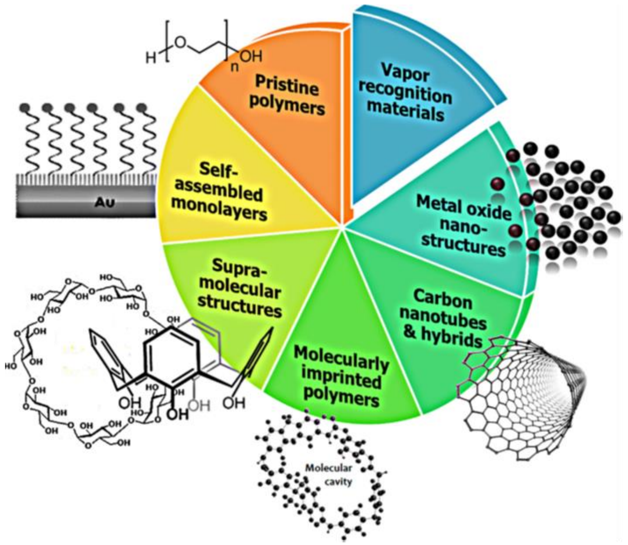
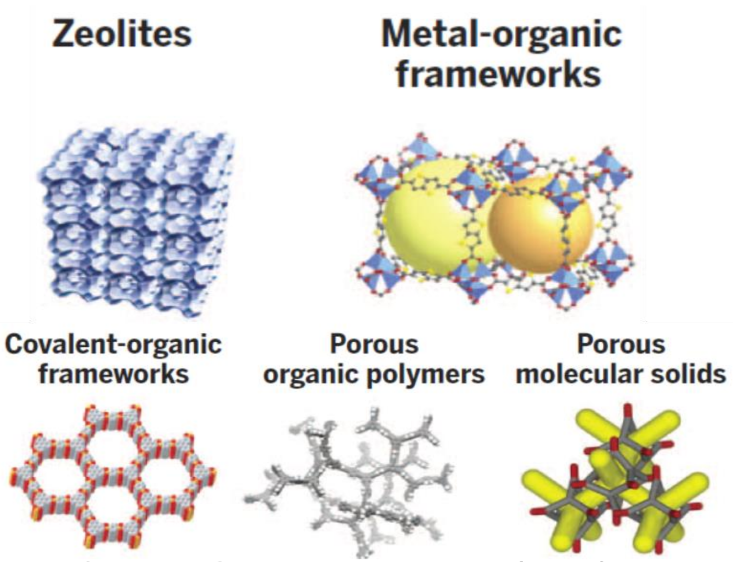
Popular vapor sensing materials for acoustic devices



Afzal et al., Anal. Chim. Acta 787 (2013) 36– 49

- Metal oxides, semiconductors
- Metals
- Polymers
- Graphene, carbon nanotubes
- Composite/hybrid materials

Porous materials?



Slater et al., Sci. 348, aaa8075 (2015)

- **Key component for sensor's performance**
- Interaction with analytes: physisorption/chemisorption
- Coupling with transducers: adhesion, other interfacial properties

Integration challenges include the high quality film formation on transducers and understanding the coupling with gases and transducers.

MOFs as Potential Sensing Layers for SAW Devices

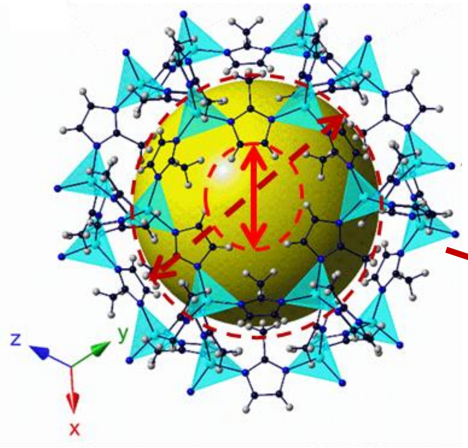
MOFs:
Non-Conducting (mostly) and stiff
High gas adsorption capacity and tunable pores

Example: **ZIF-8 MOF**

- Known structural and gas adsorption properties
- Simple, solution-based processing
- Low water adsorption

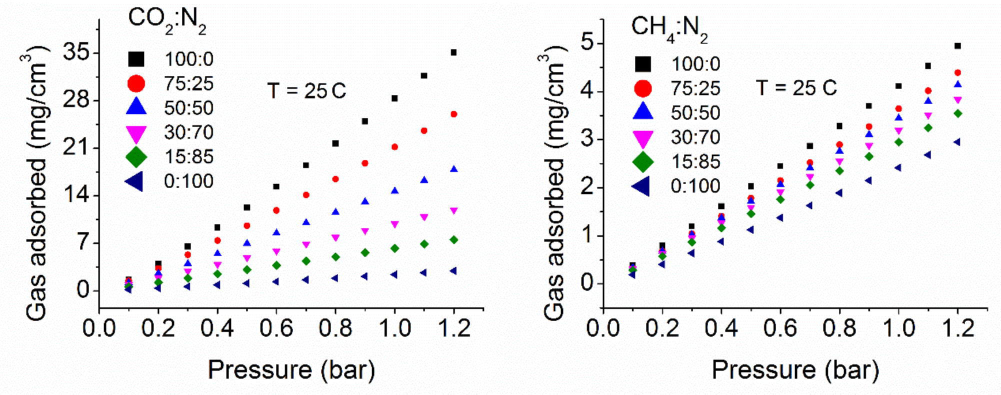
Kinetic Diameters of CO_2, CH_4, N_2: 3.3A, 3.8A, 3.7A

Pore size: ~ 11.6A

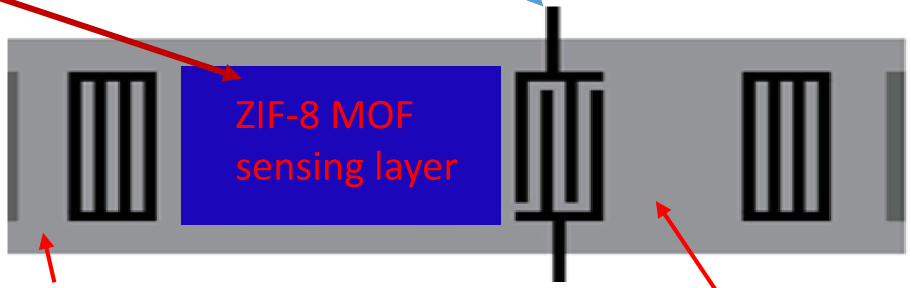


Aperture: ~ 3.4A

ZIF-8 - Gas adsorption isotherms



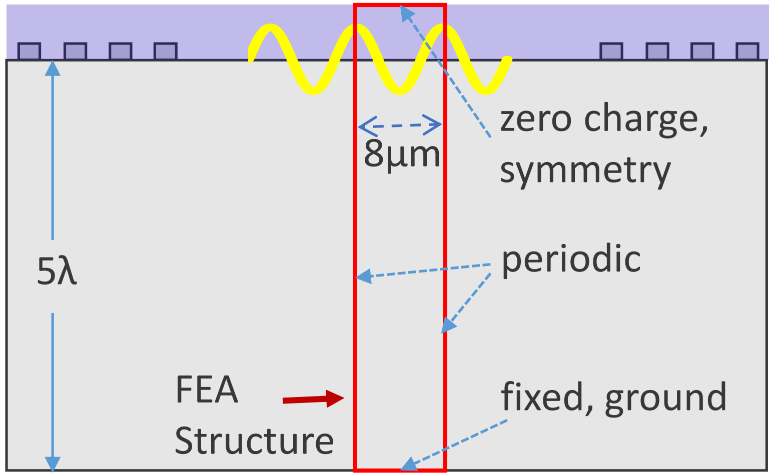
Antenna for wireless interrogation



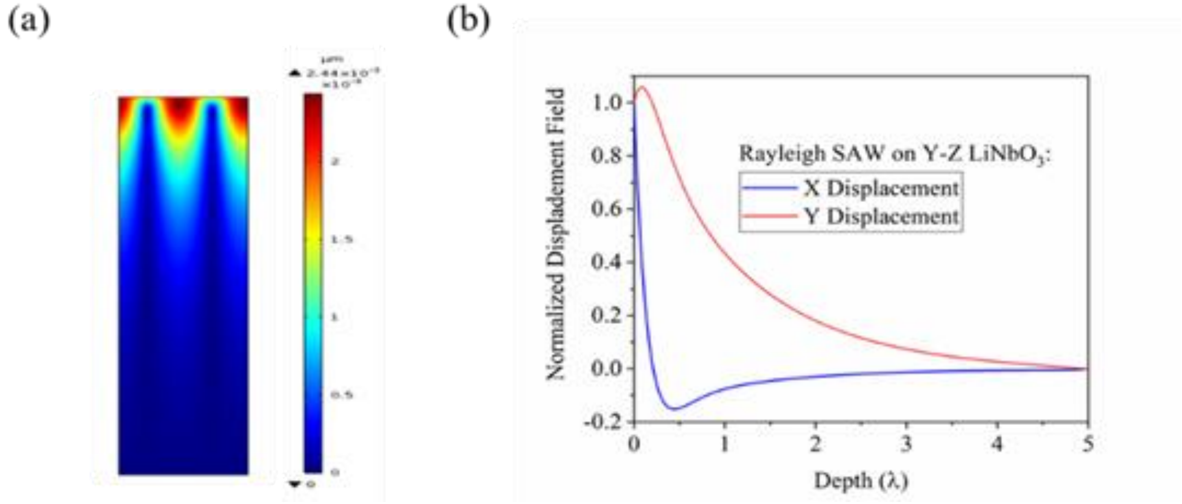
Y-Z $LiNbO_3$

Reference delay line

Finite Element Analysis of SAW Devices with ZIF-8 Layer



Displacement on free surface



Predicted f_0 = 436.27 MHz

Y-Z LiNbO3:

SAW velocity = 3487.8 m/s

(parameters from COMSOL's inbuilt library)

ZIF-8 parameters from literature

- The ZIF-8 mass density change upon gas adsorption was modeled as

$$\rho_{net} = \rho + \Delta\rho = \rho + \boldsymbol{K}C_v$$

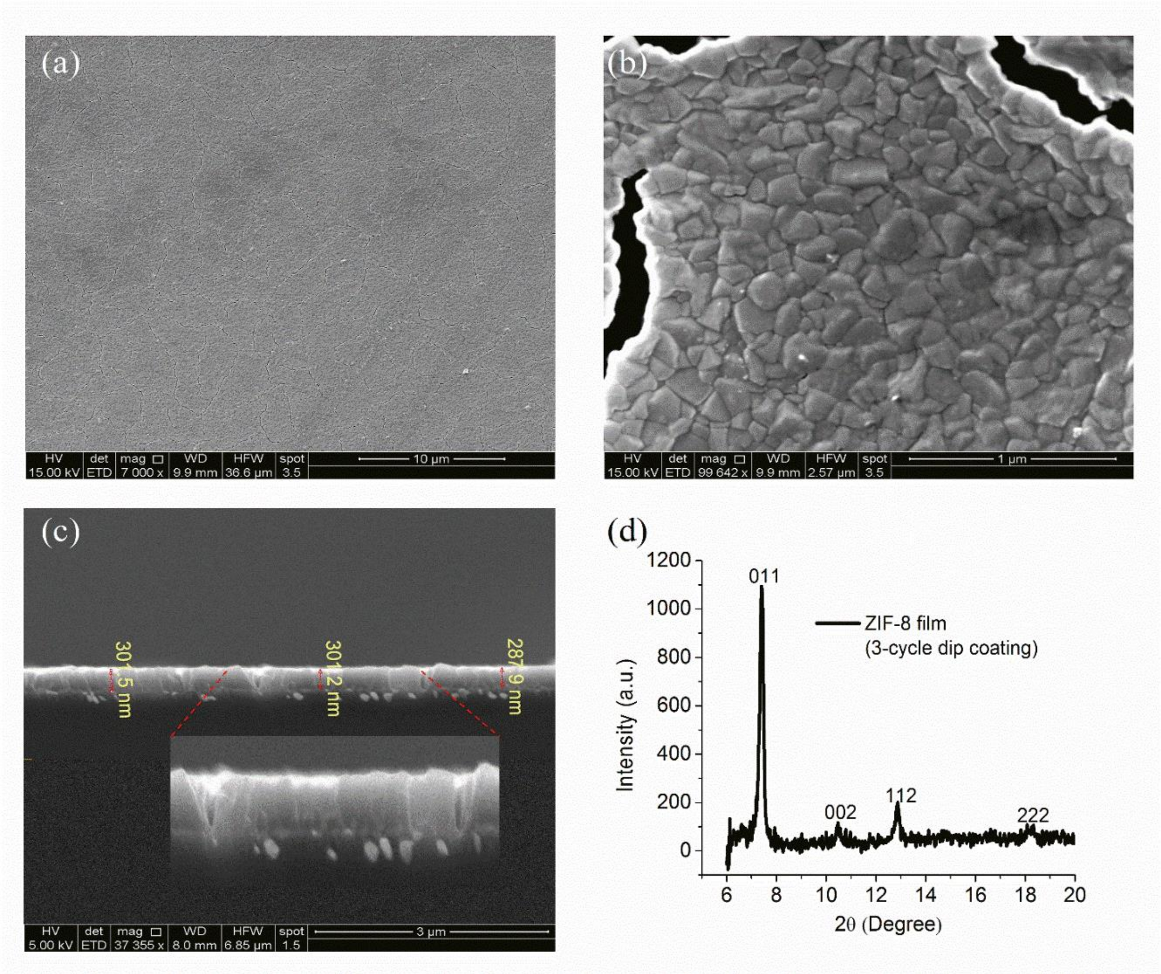
- Dimensionless Henry's constant as the partition coefficient $\boldsymbol{K} = \frac{C_s}{C_v}$.

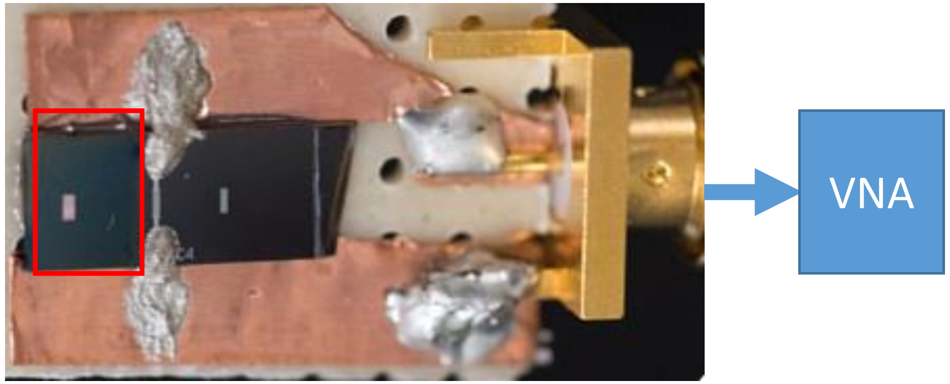
Modeling gas sensing response:

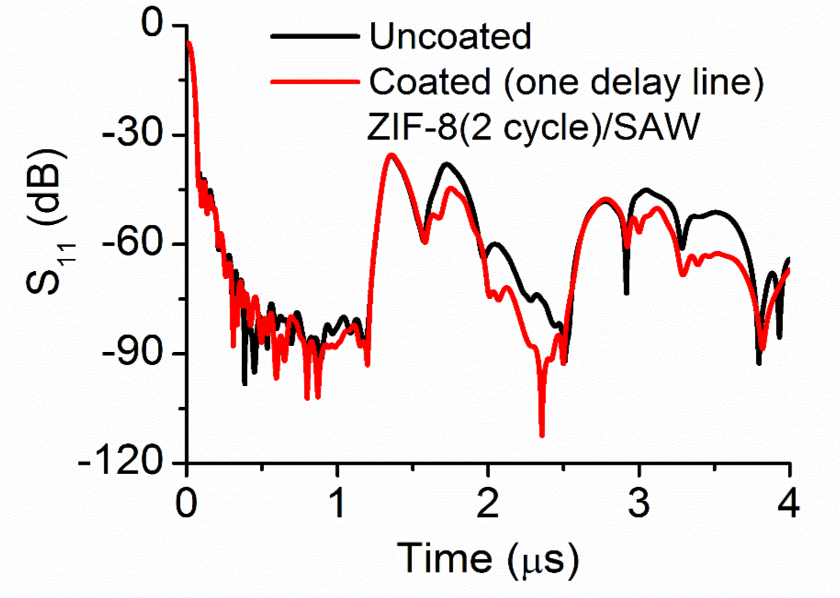
Predicted $\frac{\Delta v}{v}$ =189.3 X 10^{-6} and 25.6 X 10^{-6} for pure CO_2 and CH_4, respectively with **200 nm ZIF-8 layer**.

Integration of ZIF-8 with SAW/QCM Devices

One cycle of dip coating produces 100 nm thick ZIF-8 layer

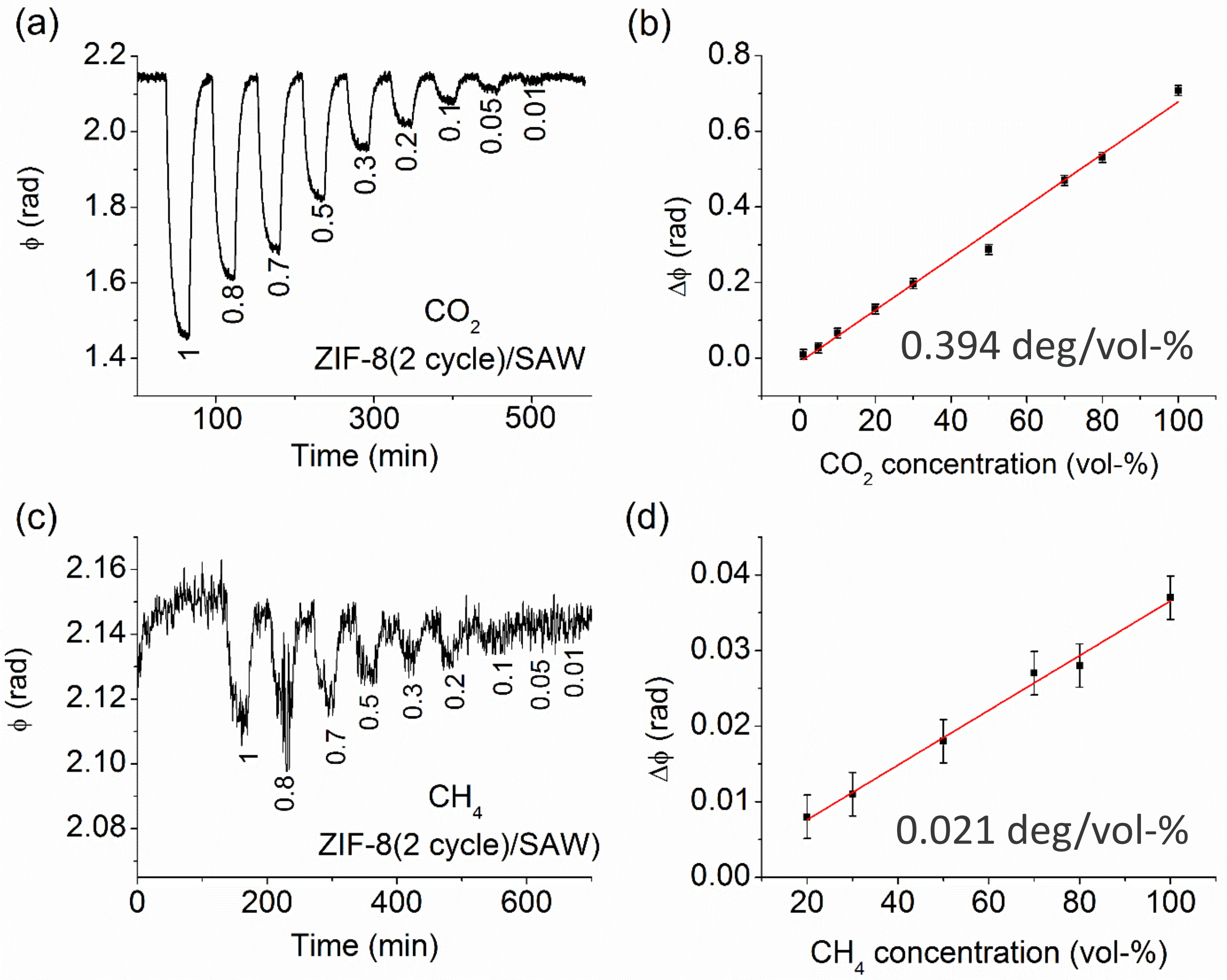


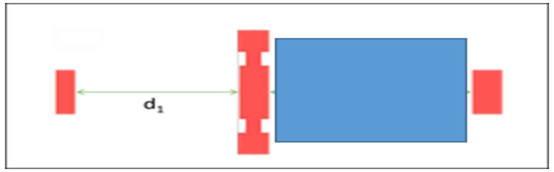




SAW delay line coated with 200-nm thick ZIF-8

ZIF-8 SAW Delay Line for CO_2 and CH_4





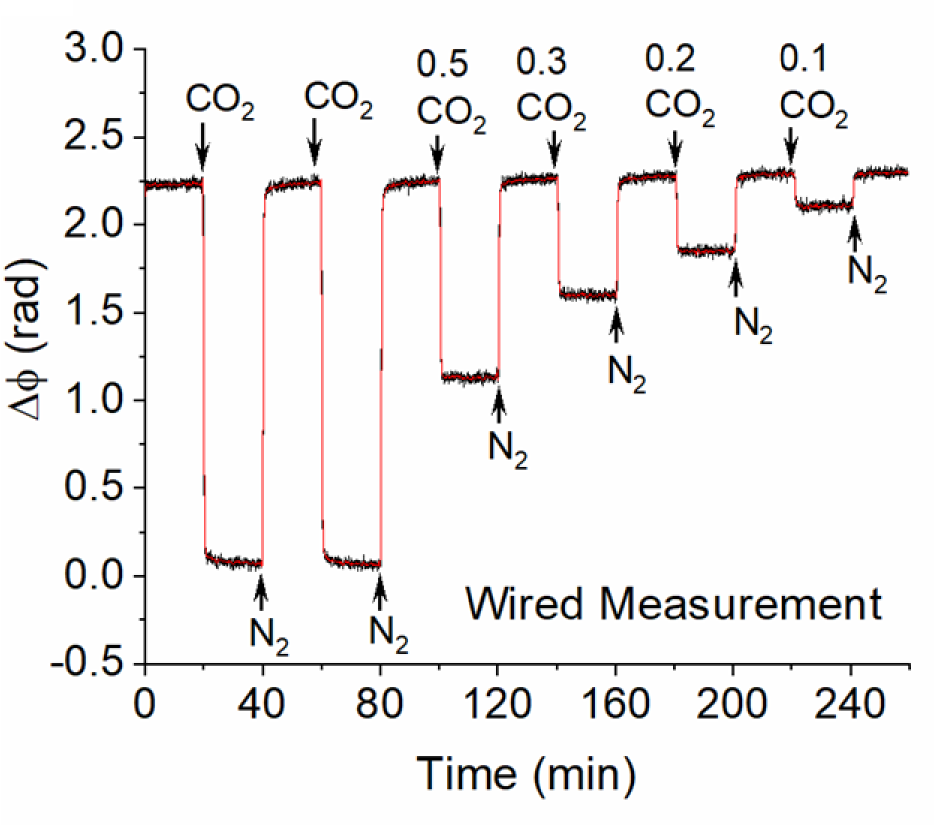
Specifications:

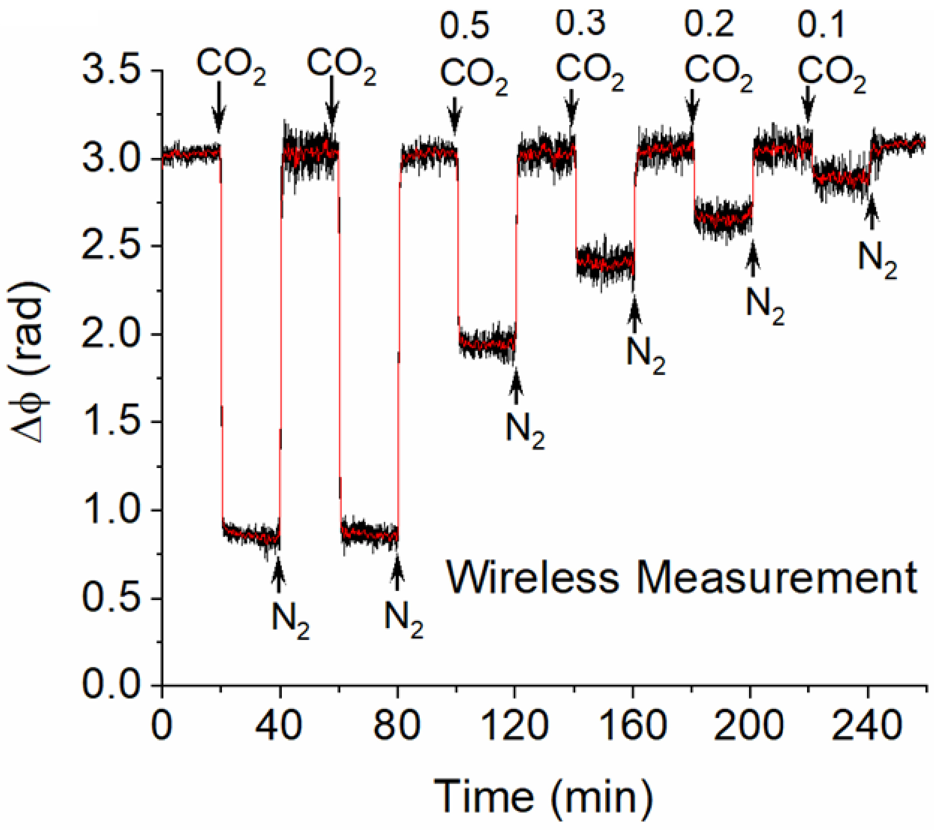
- One port delay line
- Center frequency, f_0 = 431.4 MHz
- Active area: 2.464 mm^2
- **Wired measurement**

Mass uptake (mg/cm^3-vol-%)

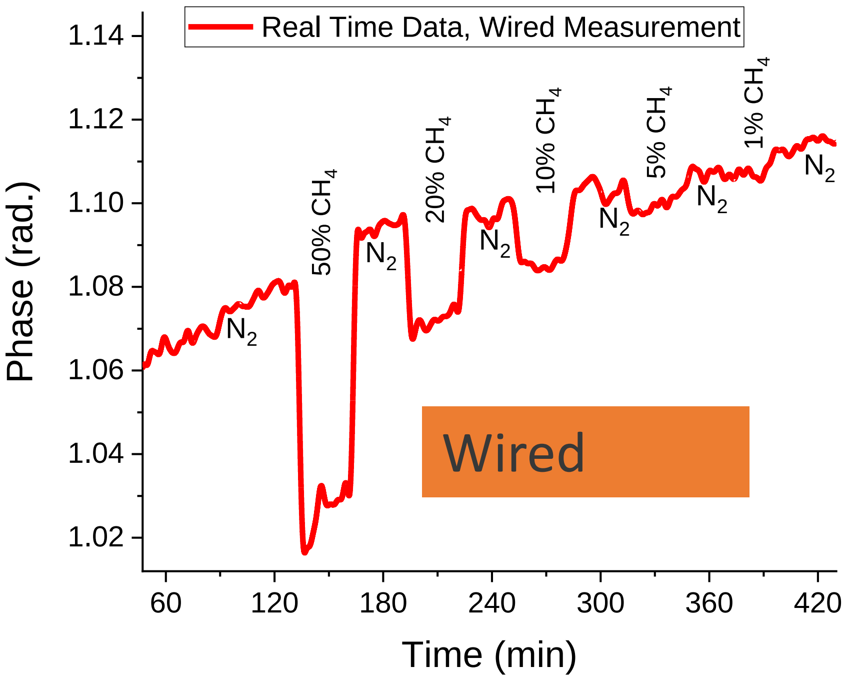
Technique	CO_2	CH_4
Gravimetric	0.257	0.015
QCM	0.595	0.025
SAW	0.304	0.016

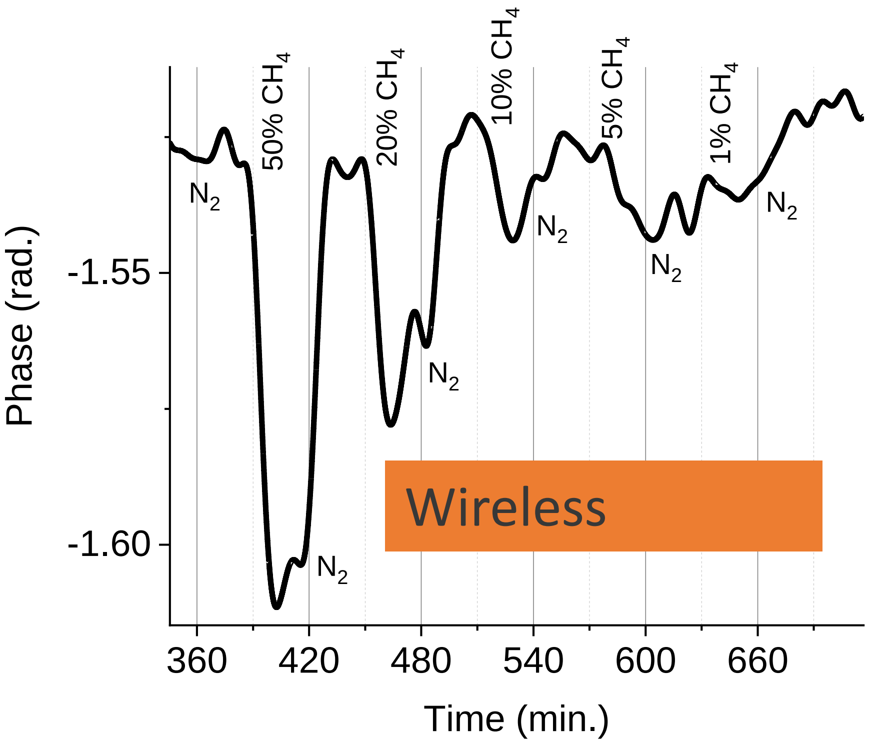
CO_2 Wireless Detection (ZIF-8/SAW)





CH_4 Wireless Detection (ZIF-8/SAW)





Challenges:

- Improvement in Sensor Sensitivity
- Noise Reduction in Wireless Measurement

Summary

- ✓ Surface acoustic wave (SAW) technology is being explored for monitoring natural gas infrastructures with the emphasis on chemical sensing.
- ✓ Demonstrated the potential of applying a novel class of nanoporous materials, metal-organic frameworks (MOFs) as sensing layers on SAW devices for greenhouse gas detection.
- ✓ Demonstrated the wired and wireless detection of carbon dioxide and methane a MOF-coated SAW sensor.
- ✓ Potential of multiple MOFs for simultaneous detection of carbon dioxide and methane using SAW sensors has been explored through finite element modeling.

Acknowledgement

NATIONAL ENERGY TECHNOLOGY LABORATORY

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