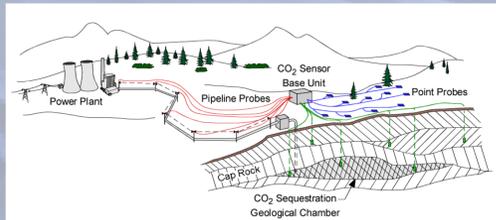


# Downhole Optical Sensor for Detecting CO<sub>2</sub> in Brine

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## Laser-based Sensors for GCS MVA and Safety

- Open-path CO<sub>2</sub> gas sensors (red) ( and below)
- Handheld / mobile leak survey tools (and below)
- Shallow in-ground CO<sub>2</sub> gas point sensors (blue)
- Well-depth supercritical CO<sub>2</sub> sensors (green) (this project)

## Open-path Sensor (OPS)

- Alarm-type system with 100-m path length
- Solar powered, with continuous monitoring via radio modem
- Intended for use along pipelines and wellhead infrastructure



Aerial view of OPS installation at IBDP injection wellhead in Decatur, Illinois

## Remote Carbon-dioxide Leak Detector (RCLD)

- Compact, portable, personnel-wearable laser module with hand-held transceiver
- Battery powered with optional data logging via RS-232 port.
- The RCLD (photo right) was laboratory tested to show its response to CO<sub>2</sub> plumes and field tested to illustrate its effectiveness around a CCS site using various objects as targets



A Heath Remote Methane Leak Detector (RMLD) was modified to detect carbon-dioxide levels by replacing the laser module, and the infrared detector with devices operating at 2.0 μm.

## Laser-based Sensors in the Broader Energy Industry

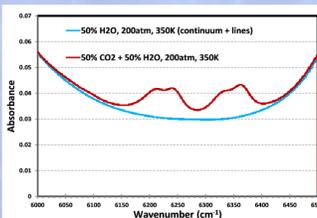
- Hand-held natural gas leak survey – Remote Methane Leak Detector (RMLD)<sup>TM</sup> – Manufactured and Distributed by Heath Consultants Inc.
- Airborne and vehicle-borne pipeline leak survey
- Autonomous methane emissions monitoring over critical facilities and leak rate quantification – ARPA-E MONITOR program
- Methane monitoring in coal mines
- Multispectral monitoring of well fluids



## TDLAS Principles

Tunable diode laser absorption spectroscopy (TDLAS) can be used to measure concentrations of CO<sub>2</sub> in any fluid phase. Carbon dioxide absorbs infrared light in specific wavelength bands (ro-vibrational transitions). A modulated laser diode current results in intensity and wavelength modulation. The diode wavelength modulation is generally centered on a CO<sub>2</sub> absorption feature away from the absorption bands of interfering molecules. However, high density water (high P gas or liquid) has a strong, broad continuum that is difficult to avoid. The figure right illustrates absorbance (A) spectra for high pressure gaseous CO<sub>2</sub> and H<sub>2</sub>O for a 10mm optical path through the fluid at the wavelength region of interest for this work. [Optical transmission  $T = I/I_0 = e^{-A}$ ]

At liquid conditions, absorbance increases to  $A_{H_2O} \sim 10$  for a 10mm path. This is still a suitable return power fraction ( $5 \times 10^{-5}$ ) to detect the  $A_{CO_2} \sim 0.05$  feature. Also, the very broad spectral width of the liquid CO<sub>2</sub> feature ( $\sim 30cm^{-1}$ ) necessitates a novel laser tuning approach that generates  $\sim 30cm^{-1}$  of wavelength tuning (over the standard  $1cm^{-1}$  approach).



## PSI Physical Sciences Inc.

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### Who we are

- A growing 42 year-old company of ~180 talented scientists, engineers and administrative personnel
- Headquartered in Andover, MA, with eight satellite locations in the U.S.
- Three wholly-owned subsidiaries, Q-Peak, Research Support Instruments, Faraday Technology, with complementary capabilities
- A technologically diverse research and development organization with revenues of nearly \$50M
- Employee-owned through an Employee Stock Ownership Trust

### What we do

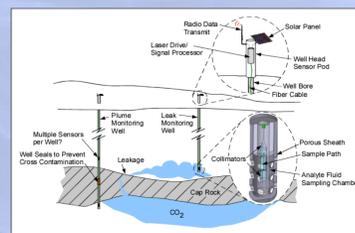
- Applied contract research and development for all major agencies of the U.S. government
- Technology development under contract to both industry and government
- Prototype product development for industry and commercial applications
- Components, systems, and instrumentation for industry and government sales
- Technology and product licensing

### PSI Industrial Sensors

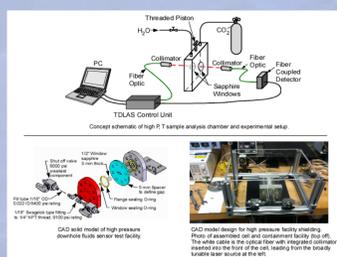
- Interdisciplinary combination of science and engineering skills with specific strengths in development and commercialization of photonic sensors and instrumentation
- Product development from concept to manufacturing prototype
- Go to market via direct sales, strategic partnerships, pilot scale manufacturing, and licensing
- Developing strong interactions with the oil & gas and broader energy industries since 1994

## Abstract

PSI is developing a sensor, based on tunable diode laser absorption spectroscopy (TDLAS), for continuous and autonomous in situ measurement of fluids within and around sequestration reservoirs for CO<sub>2</sub> content. The sensor employs broad spectral tuning of a near-infrared laser to access vibrational absorption bands of supercritical and gaseous CO<sub>2</sub> in the presence of reservoir water. The fluid interrogation is accomplished via a passive optical sensor head at depth that is coupled to the laser at the surface (well head) via an optical fiber. A field test prototype design is presented, along with initial laboratory results from a benchtop proof-of-concept apparatus. The sensor supports geological carbon sequestration (GCS) monitoring, verification, and accountability (MVA) needs for detecting and characterizing leakage from GCS sites at all depths. A suite of downhole sensors can also help advance the science of GCS fluid transport modeling by monitoring CO<sub>2</sub> plume progress cost effectively with speed, sensitivity, and chemical selectivity to supplement current techniques of seismic mapping and pulsed neutron decay.



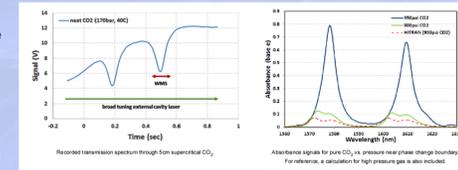
## High P & T Lab Test Facility



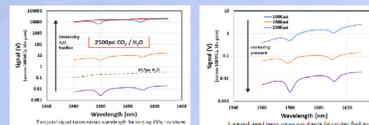
- Sapphire-windowed optically-accessible sample chamber
- In-line manual pump to 3500psi (replaces threaded piston in Figure)
- Secondary containment for protection
- Two spacers fabricated at 5mm and 50mm thickness (optical path length)
- H<sub>2</sub>O / CO<sub>2</sub> mixtures generated by injecting water first then pressurizing with CO<sub>2</sub>. CO<sub>2</sub> diffuses in or is elevated with partial sample removal and successive dilution with CO<sub>2</sub>

## Signal Measurement

- Fiber-coupled input can be telecom distributed feedback (DFB) diode laser or wide spectral range external-cavity diode laser (employed by all data shown here). ECDL also has a wavelength monitor reference signal.
- Wide wavelength (275cm<sup>-1</sup>) sweep (ECDL) employed to reveal full spectral range of features. (30cm<sup>-1</sup> telecom source is specified for final sensor wavelength modulation spectroscopy "WMS" measurement)
- Variable gain on detector employed to accommodate wide range of H<sub>2</sub>O mixture fraction (broadband attenuation)
- Phase change illustrated from double-lobed high-density gas spectral feature to single-peaked liquid feature

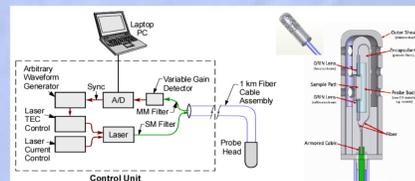


## Results vs. P and Mixture Fraction



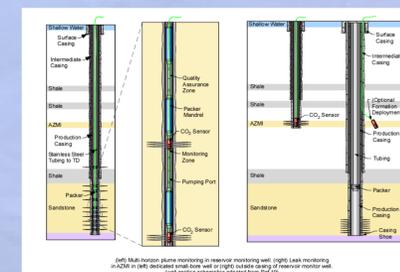
- 10<sup>6</sup> dynamic range demonstrated. Illustrates water absorption is closer to 3/cm ( $e^{-2.8cm^{-1}5cm} \approx \sim 10^6$ ). Also, smallest signal on plot (0.01V) (strongest attenuation) is equivalent to  $\sim 1pW$  on the detector.
- Broadband attenuation increases with pressure and H<sub>2</sub>O content
- CO<sub>2</sub> features observable through wide range of broadband attenuation.

## Engineering Prototype Design



- Passive optical probe head with porous outer sheath
- Few cm fiber-optically coupled path fixed by an encapsulant
- Rugged fiber cable with delivery and return fiber
- Electronics at surface in shoe box-sized Control Unit connected to PC for R&D or telemetry hardware for autonomous operation.

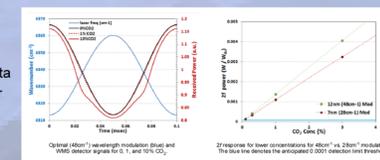
## Concept of Operations



- Deployed in reservoir monitor well at potentially multiple depths with single cable
- Deployed in porous "leak-monitoring" layer (above-zone monitoring interval (AZMI))

## WMS Sensor Modeling

- Liquid CO<sub>2</sub> feature approaches Lorentzian line shape
- Available modulation depth (28cm<sup>-1</sup>) approaches optimal modulation depth (2.2FWHM, 48cm<sup>-1</sup>).
- Model system response using 28cm<sup>-1</sup> wide portion of recorded absorption data
- Relatively insensitive to modulation depth. 28cm<sup>-1</sup> modulation only 25% lower response than optimum depth.
- The approach will be sufficient. 10<sup>-4</sup> absorbance detection limit is near 0.1% CO<sub>2</sub>.



## Extension Applications

- Enhanced oil recovery (EOR) – plume monitoring, multi-horizon on/off production and phase control, broadband NIR optical fluid analysis...
- Enhanced (natural) gas recovery (EGR) and CO<sub>2</sub>-based hydraulic fracturing – plume, leak, and production path monitoring
- Logging while drilling
- Monitoring natural CO<sub>2</sub> reservoirs
- Factory supercritical CO<sub>2</sub> applications (solvent, refrigerant, reagent...)
  - CO<sub>2</sub> as extracting solvent (coffee decaffeination, botanical oils...)
  - Rapid CO<sub>2</sub> expansion for microparticulation (pharma & more)

## Conclusions

- Supercritical CO<sub>2</sub> spectral signatures observed across >10<sup>6</sup> dynamic range of broadband attenuation (from H<sub>2</sub>O)
- Wide modulation WMS approach sufficient at all P & T conditions
- Detection limits for a 5cm path estimated at <0.1% CO<sub>2</sub>
- Engineering prototype is designed – in follow-on work, build and test (immersed probe head) in lab and field test

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