Laser based Chemical Sensor Technology: Recent Advances and Applications

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http://ece.rice.edu/lasersci/

OUTLINE

UDLA 2007
Puebla, Mexico
June 11, 2007

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New laser sources and sensing technologies
- Selected Applications of Trace Gas Detection
  - Detection of formaldehyde and nitric oxide
  - Volcanic gas emission studies
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
- Future Directions and Conclusions

Work supported by NSF, NASA, DOE, DoD and Robert Welch Foundation

Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing & Food Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medicine and Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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International Space Station

Worldwide Megadirty Mega Cities

	Population, m 1990, est.	2000, proj.	Sulphur dioxide	Particulate matter	Lead	Carbon monoxide	Nitrogen dioxide	Ozone
Bangkok	7.16	10.26	O	●	Ø	O	O	O
Beijing	9.74	11.47	●	●	O	-	O	Ø
Bombay	11.13	15.43	O	●	O	O	O	-
Buenos Aires	11.58	13.05	-	Ø	O	-	-	-
Cairo	9.08	11.77	-	●	●	Ø	-	-
Calcutta	11.83	15.94	O	●	O	-	O	-
Delhi	8.62	12.77	O	●	O	O	O	-
Jakarta	9.42	13.23	O	●	Ø	Ø	O	Ø
Karachi	7.67	11.57	O	●	●	-	-	-
London	10.57	10.79	O	O	O	Ø	O	O
Los Angeles	10.47	10.91	O	Ø	O	Ø	Ø	●
Manila	8.40	11.48	O	●	Ø	-	-	-
Mexico City	19.37	24.44	●	●	Ø	●	Ø	●
Moscow	9.39	10.11	-	Ø	O	Ø	Ø	-
New York	15.65	16.10	O	O	O	Ø	O	Ø
Rio de Janeiro	11.12	13.00	Ø	Ø	O	O	-	-
Sao Paolo	18.42	23.60	O	Ø	O	Ø	Ø	●
Seoul	11.33	12.97	●	●	O	O	O	O
Shanghai	13.30	14.69	Ø	●	-	-	-	-
Tokyo	20.52	21.32	O	O	-	O	O	●

Source: United Nations ● High pollution Ø Moderate to heavy pollution O Low pollution - No data available

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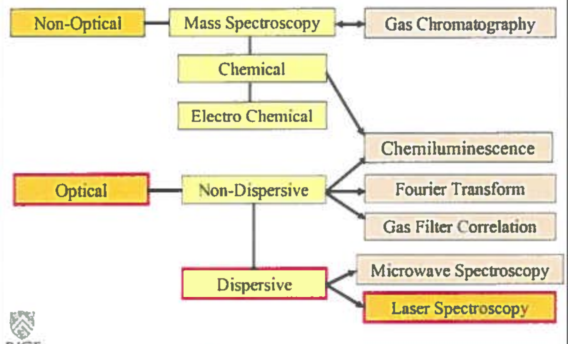
Megacity Air Pollution: Houston, TX

Trace Gas Monitoring in a Petrochemical Plant

University of Szeged, Hungary

Popocatepetl, Mexico (December 1994)

Existing Methods for Trace Gas Detection



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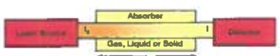
Fundamentals of Laser Absorption Spectroscopy

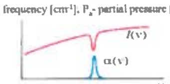


Beer-Lambert's Law of Linear Absorption

$I(\nu) = I_0 \, e^{-\alpha(\nu) P_a L}$

$\alpha(\nu)$ - absorption coefficient [cm^{-1} atm^{-1}], L - path length [cm]

ν - frequency [cm^{-1}], P_a - partial pressure [atm]



$\alpha(\nu) = C \; S(T) \; g(\nu - \nu_0)$

C - total number of molecules of absorbing gas/atm cm^3 [molecule cm^{-3} atm^{-1}]

S - molecular line intensity [cm molecule^{-1}]

$g(\nu - \nu_0)$ - normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Requirements: Sensitivity, specificity, multi-gas species, rapid data Acquisition, ...

Optimum Molecular Absorbing Transition
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

Long Optical Pathlengths
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

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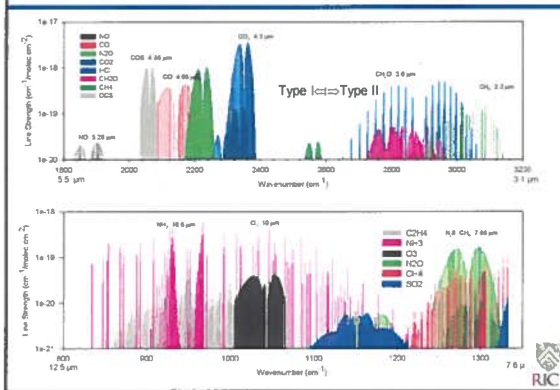
HITRAN Simulation of Absorption Spectra



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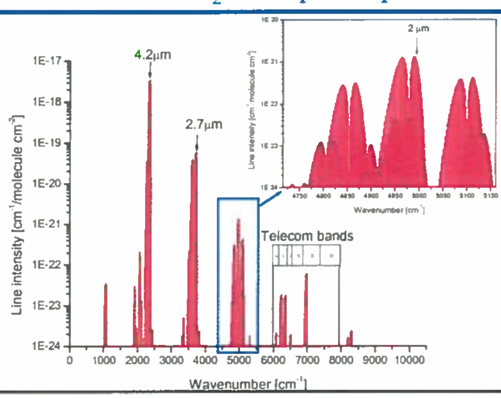
Simulated CO_2 Absorption Spectrum



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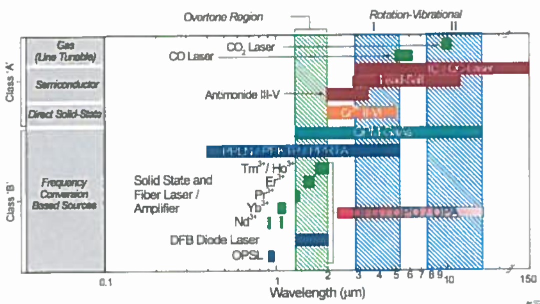
Mid-IR Source Requirements for Laser Spectroscopy

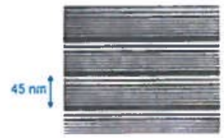
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

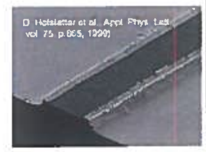
IR Laser Sources and Wavelength Coverage



Quantum Cascade Laser: Basic Facts

- Semiconductor lasers (III-V materials)
- Multiple-quantum-well heterostructure
- Intersubband transitions
- Band-structure engineering (emission wavelength defined by the layer thickness – MBE, MOCVD etc.)
- Independent of material energy bandgap
- Cascading (each electron creates N laser photons)
- Number of periods N determines laser power
- High reliability, long lifetime
- Compact

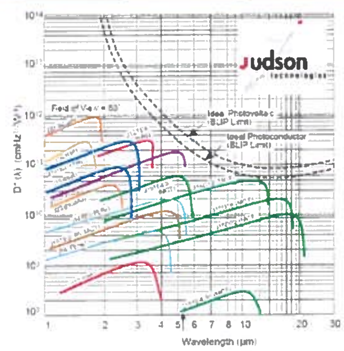




Key Characteristics of Mid-IR QCLs and ICLs

- Laser wavelengths cover the entire Mid-IR range from 3 to 24 µm
- High power (>500 mW cw, >5W peak for pulsed)
- High spectral purity - single frequency with DFB structure or external cavity
- Continuous tuning by temperature (~10 cm^{-1}) or current (~1 cm^{-1}) or external cavity (>200 cm^{-1} → pulsed mode)
- High reliability: low failure rate, long lifetime and robust
- Capable of room temperature operation
  - Pulsed: up to +150°C
  - CW: up to RT

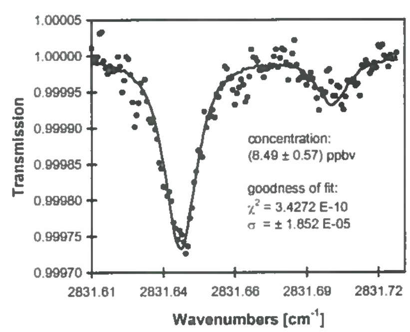
Wavelength Coverage of IR Detectors



Motivation for Monitoring of H_2CO

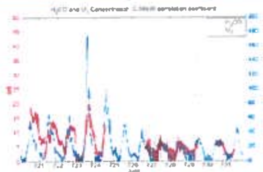
- Toxic pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products (eg. resins, foam)
- Atmospheric H_2CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas

H_2CO Detection in Ambient Air at 3.53 µm



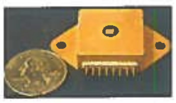
D. Rehle et al. Applied Physics B72, 947-952 (2001)

DFG and ICL based H_2CO Sensor for studying Urban Air Pollution



H_2CO & O_3 concentrations at Deer Park (2003)

Rice DFG system (2003)

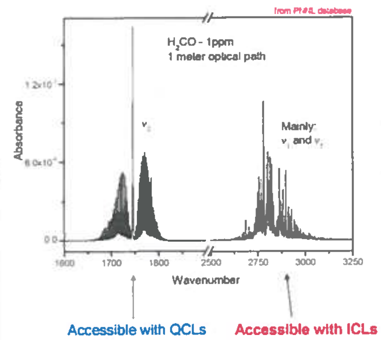


JPL 3.3 μm cw TEC cooled ICL (2007)

Rice dual ICL system (2006)

NCAR DFG system (2007)

Detection of Formaldehyde



No significant difference in line intensity between the vibrational band ν_2 (C–O stretch) at 5.7 μm and bands ν_1 and ν_5 (C–H stretches) at 3.6 μm

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TexAQS II Field Campaign Summer 2006

- To study ozone formation and transport, a coordinated field study was conducted in August and September 2006 in Houston
- 5 aircraft, two ground chemistry sites, ~20 periphery and meteorological sites
- Participation by~300 scientists from academia, national laboratories, industry and government

Moody Tower, UH Campus

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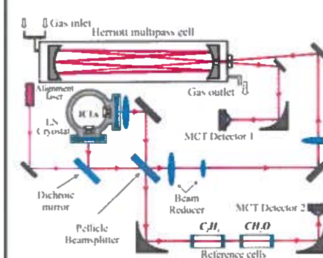
Dual CW ICL Based Trace Gas Sensor for TexAQS '06

Measurement technique:

- Two CW DFB ICLs
- 100 m Herriott multipass cell
- Both laser beams co-aligned with a 50/50 beam splitter
- Two optical channels and two detectors:
  - Signal
  - Reference (quasi line locking)
- Wavelength modulation (2f)
- Phase sensitive detection at two different modulation frequencies (4 lock-in amplifiers, 2 for each channel)
- Concentration measurement by linear least squares fitting of the pre-acquired reference spectrum (calibration mixture) to the sample spectrum



- Automatic self-calibration
- Automatic LN_2 refilling system
- Remote operation

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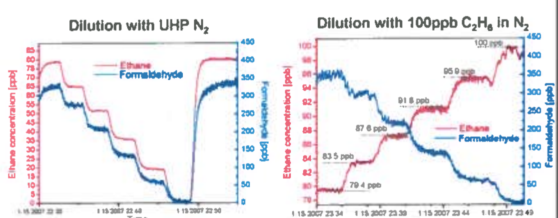
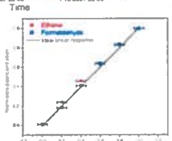
Sensor Performance – Two Channel Detection



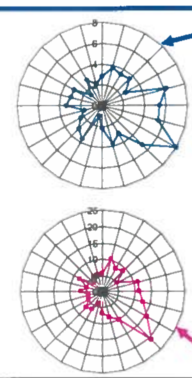
Custom mixture:
- ~79 ppb of C_2H_6
- ~330ppb of H_2CO
- N_2 as a buffer gas



- Linear response of the sensor
- No cross-talk between channels
- C_2H_6 sensitivity: ~150 ppt (1σ) in 1 sec
- H_2CO sensitivity: ~3.5 ppb (1σ) in 1 sec

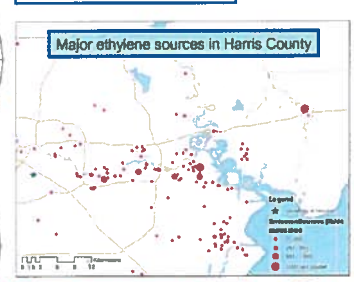
Wysocki et al "Dual Interband Cascade Laser based Trace Gas Sensor for studying Urban Air Pollution" Photonics West 2007

H_2CO concentration (ppb) versus Wind Direction



Mean H_2CO concentration versus wind direction at sampling site (conc. in ppbV)

Max H_2CO concentration versus wind direction at sampling site (conc. in ppbV)



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Ron Brown Ship Track, August 2006

Aerodyne Inc., Billerica, MA

Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1988 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection

NO as a Biomarker

- NO is biochemically involved in most tissues and physiological processes in the human body
- NO excretion increases in exhaled breath in lung diseases such as :
  - ✓ Asthma[1]
  - ✓ Chronic Obstructive Pulmonary Disease[2]
  - ✓ Acute lung rejection[3]
  - ✓ Acute respiratory distress syndrome[4]
  - ✓ Pneumonia (useful for intubated patients)[5]

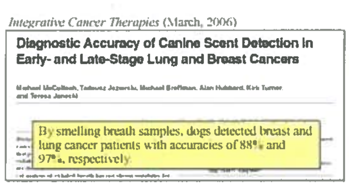
[1] Alving K, E Weitzberg, JM Lundberg. Increased amount of NO in exhaled air of asthmatics. Eur Respir J 1993, 6: 1368-1370
[2] Wasem M, S Loukides, S Culpitt, P Sullivan, S Kharitonov, P Barnes. Exhaled NO in COPD. Am J Respir Crit Care Med 1998, 157: pp 998-1002
[3] Silkoff PE et al. Exhaled NO in human lung transplantation. A noninvasive marker of acute rejection. Am J Respir Crit Care Med 1998, 157(6): 1822-1828.
[4] Brett SJ, Evans TW. Measurement of endogenous NO in the lungs of patients with the ARDS. Am J Respir Crit Care Med 1998, 157 (3 Pt 1): 993-7.
[5] Adrie C et al. Exhaled and nasal NO as a marker of pneumonia in ventilated patients. Am J Respir Crit Care Med 2001; 163(5):1143-9

Why is Breath so Useful ?

- Breath can be analyzed non-invasively from spontaneously breathing human subjects (neonate to the elderly), laboratory animals (from mice to horses), or from intubated patients (in ORs or ICUs).
- Breath can be sampled in the clinic, the home, the field, at the patient bedside, or in the physician's office by nurses, technicians, physicians and by the patient themselves.
- Breath analysis can be used for nutritional studies, exercise studies, to detect disease, stage disease, to monitor therapy or to monitor treatment

Terence Risby, Johns Hopkins University

Dogs Can Smell Cancer



Integrative Cancer Therapies (March, 2006)

Diagnostic Accuracy of Canine Scent Detection in Early- and Late-Stage Lung and Breast Cancers

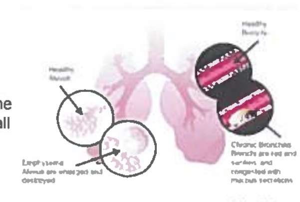
By smelling breath samples, dogs detected breast and lung cancer patients with accuracies of 88% and 97%, respectively.

The evidence is clear – gas phase molecules are uniquely associated with cancer

– We need sensors that can detect these biomarkers

Chronic Obstructive Pulmonary Disease

- **Chronic obstructive pulmonary disease (COPD)**
  - Accumulation of inflammatory products in the small airway lumen and wall
- **Alveolar NO**
  - Reflects peripheral lung inflammation and the response to anti-inflammatory treatment
  - Not affected by smoking or inhaled corticosteroids



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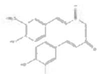
Curcumin Pilot Study

- Curcumin (Turmeric)
  - Polyphenol (diferuloylmethane)
  - Anti-inflammatory and anti-oxidant



- **Hypothesis:** Curcumin reduces indices of inflammation in individuals with severe COPD

BCM

Collaborator: Dr. Amir Sharafkhaneh

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Breath Biomarkers in Humans

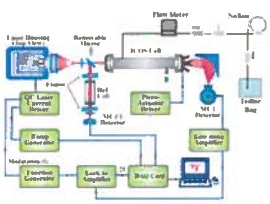
As many as 400 different molecules in breath, many with well defined biochemical pathways

BROADBAND ABSORBERS

Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm	Decarboxylation of acetoacetate, diabetes
Ammonia	ppb	protein metabolism, liver and renal disease
Carbon dioxide	%	Product of respiration, Helicobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb	Lipid peroxidation, oxidative stress, cancer
Hydrocarbons	ppb	Lipid peroxidation/metabolism
Hydrogen	ppm	Gut bacteria
Isoprene	ppb	Cholesterol biosynthesis
Methane	ppm	Gut bacteria
Methanethiol	ppb	Methionine metabolism
Methanol	ppb	Metabolism of fruit
Methylamine	ppb	Protein metabolism
Nitric oxide	ppb	Production catalyzed by *nitric oxide synthase*
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

Terence Risby, Johns Hopkins University

Laser-based ICOS Nitric Oxide Sensor

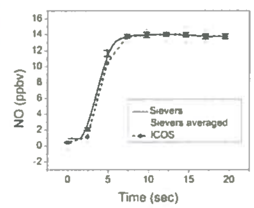


NO:N2 mixture @ 100 Torr
Effective L= 700 m

A 1σ deviation of the amplitude corresponds to a 0.7 ppb detection limit (1sec.)

Online NO concentration measurements at 3l/min exhalation.

Intercomparison of ICOS and commercial chemiluminescence sensor (Sievers – solid line)



M R McCurdy, Y Bakhirkin, G Wysocki, F K Tittel "Performance of an exhaled nitric oxide and carbon dioxide sensor using quantum cascade laser based integrated cavity output spectroscopy" to appear in Journal of Biomedical Optics 2007

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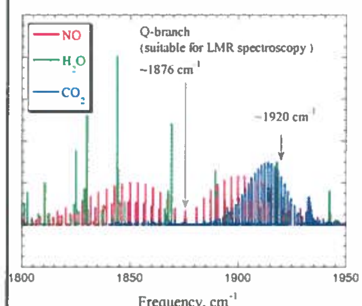
Simulated NO Absorption Spectrum



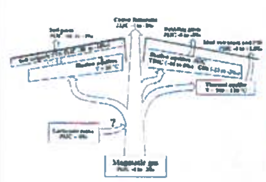
Why is it difficult to obtain a DFB-QCL at 1876 cm^{-1}?

- Absorption lines in the P and R branches are stronger and therefore more suitable for most LAS applications
- Fabrication process of a DFB is costly
- Q-branch is very narrow which additionally requires a higher precision in DFB fabrication

Volcanic Gas Emission Studies

Volcanological Applications

- CO_2 the most abundant component of volcanic gases after H_2O
- d^{13}C is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
- Monitoring d^{13}C can be used in eruption forecasting and volcanic hazard assessment



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CO_2 Absorption Line Selection Criteria

- Three strategies:
  - Similar strong absorption of $^{12}CO_2$ and $^{13}CO_2$ lines
    - Very sensitive to temperature variations
  - Similar transition lower energies
    - Requires a dual path length approach to compensate for the large difference in concentration between major and minor isotopic species-or-
    - Can be realized if different vibrational transitions are selected for the two isotopes (4.35 µm for $^{13}CO_2$ and 2.76 µm for $^{12}CO_2$)*
- For the first 2 strategies both absorption lines must lie in a laser frequency scan window
- Avoid presence of other interfering atmospheric trace gas species

* Proposed scheme by Curl, Uehara, Kosterev and Tittel, Oct. 2002

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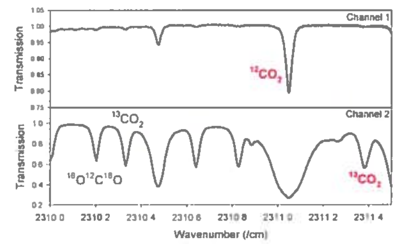
High resolution CO_2 absorption spectrum at 2311 cm^{-1}



OSAS Optics and Photonics News, May 2006

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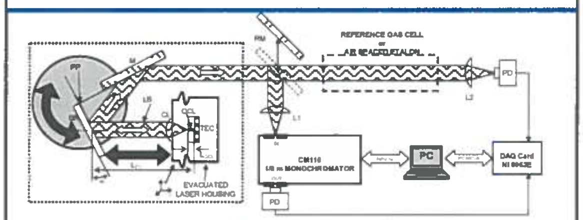
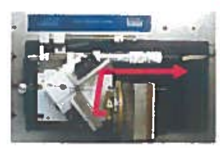
Widely Tunable, CW, TEC Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer, 2006





- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

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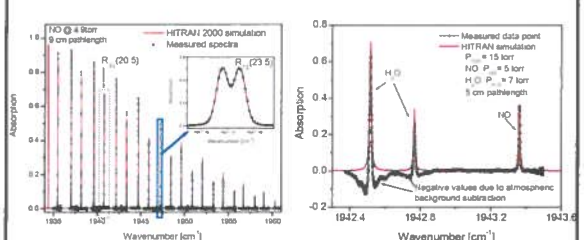
Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL



G. Wysocki, R.F. Curl, F.K. Tittel, R. Maulini, J. Faist, *Appl. Phys. B* 81, 769-777 (2005)

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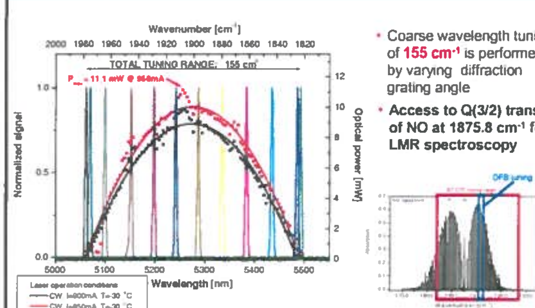
Wide Wavelength Tuning of a 5.3µm EC-QCL



- Coarse wavelength tuning of **155 cm^{-1}** is performed by varying diffraction grating angle
- **Access to Q(3/2) transition of NO at 1875.8 cm^{-1} for LMR spectroscopy**

G. Wysocki, R. F Curl, F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

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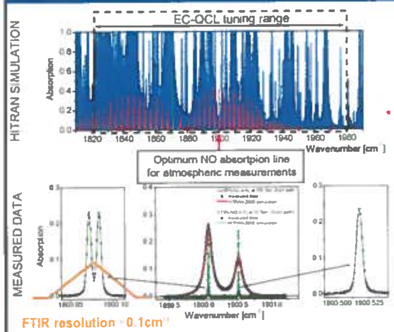
High resolution spectroscopy with a 5.3μm EC-QCL

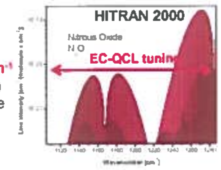


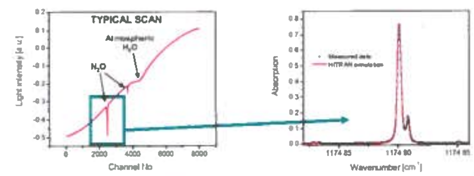
- Mode hop free scan of up to ~**2cm⁻¹** with a resolution **<0.001cm⁻¹** (30MHz) can be performed anywhere within the tuning range

G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

High resolution spectroscopy with a 8.4μm EC-QCL

- Mode hop free scan of up to ~**1.25 cm⁻¹** with a resolution **<0.001cm⁻¹** (30MHz) can be performed anywhere within the tuning range

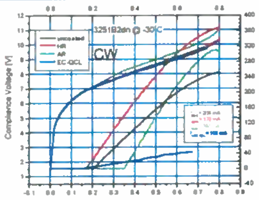


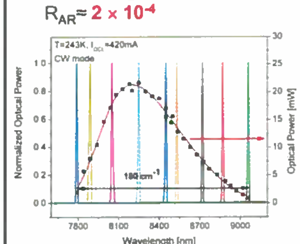


Performance of a 8.4 μm EC-QCL spectroscopic source

$P_{EC\text{-}opt}$ up to **50 mW (cw)**
(I_{QCL} = 680 mA -> P = 44 mW)

AR coating:
$R_{AR} \approx$ **2 × 10⁻⁴**



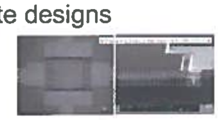


Tunability **180 cm⁻¹**
@8.4 μm (7.8μm - 9.1μm)

G. Wysocki, R. F. Curl, F. K. Tittel, F. Capasso, L. Diehl, M. Troccoli, R. Maulini, J. Faist, Optics Express (June 11, 2007)

Further development of the EC-QCL technology

- Broader wavelength tunability
- Faster tuning speed
- All Solid state designs
  - MEMS



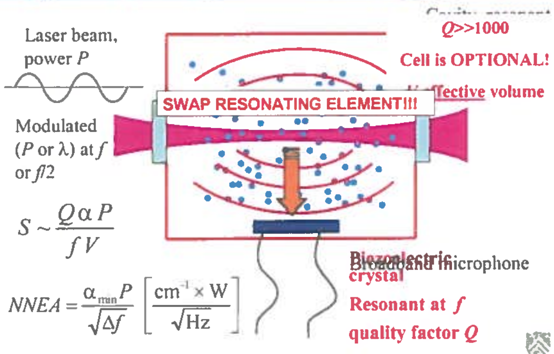
  - All electrical tuning (in collaboration with QCL-research groups)
    - Tunable Distributed Bragg Reflectors (DBR) (carrier-induced refractive index tuning)
    - Electronically tunable extraordinary transmission gratings (tunable mirrors and filters) (work presently carried out at Princeton)

Quartz Enhanced Photoacoustic Spectroscopy

First Report of PAS in 1880

Alexander Graham Bell's "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
Nature, Sept. 23, **1880**, pp. 500-503

From conventional PAS to QEPAS



$$S \sim \frac{Q \alpha P}{f V}$$

$$NNEA = \frac{\alpha_{min} P}{\sqrt{\Delta f}} \left[\frac{cm^{-1} \times W}{\sqrt{Hz}}\right]$$

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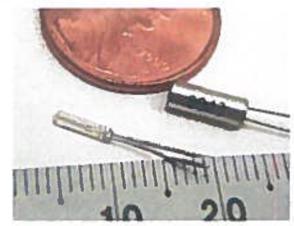
Quartz tuning fork (TF) as a resonant microphone

- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000, Q_{air}~10 000 at ambient conditions,
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for clocks – low cost



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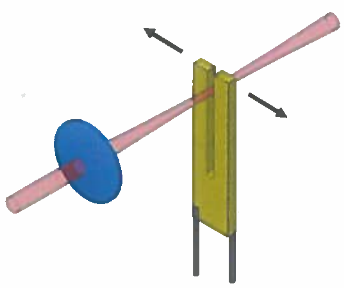
Quartz Tuning Fork based Spectrophone



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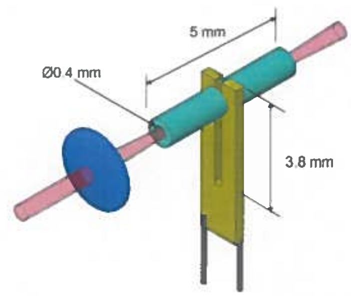
Quartz Tuning Fork based Spectrophone



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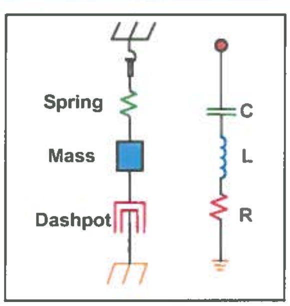
Equivalent Electrical Circuit of a Quartz TF



$$\omega_0 = \sqrt{\frac{1}{LC}}$$

$$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$$

$$\sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4 k_B T}{R}}$$

"QUARTZ CRYSTAL RESONATORS AND OSCILLATORS For Frequency Control and Timing Applications", tutorial by John R. Vig, U.S. Army Communications-Electronics Command (July 2001)

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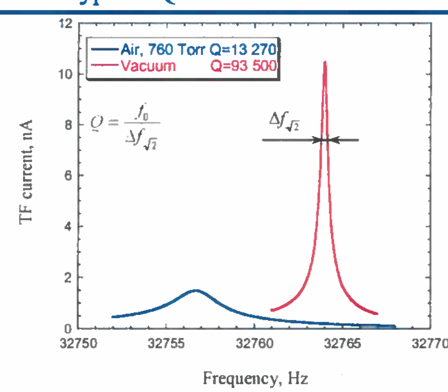
Typical QTF Resonance Curves



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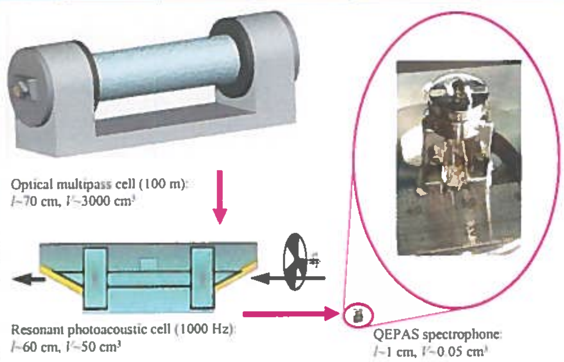
Comparative Size of Absorbance Detection Modules (ADM)



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Motivation for NH_3 Detection

- Monitoring of gas separation processes
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

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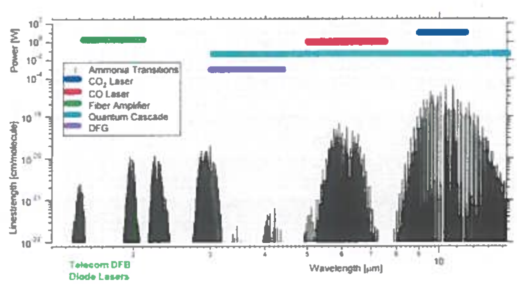
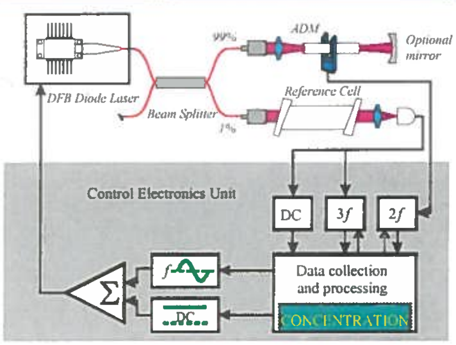
Simulated Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Pranalytica

QEPAS based Gas Sensor Architecture



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NH_3 Measurements at an Oklahoma State University Research Feedyard

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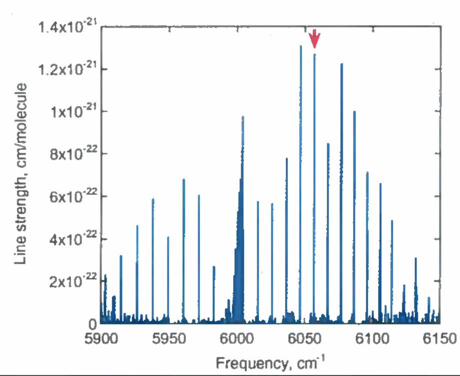
Ekips

$2\nu_3$ Absorption Band of CH_4 (HITRAN)



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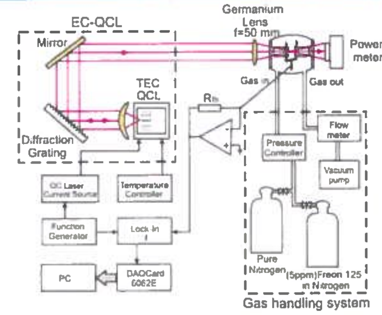
Motivation for Monitoring of Freon 125 and acetone

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (CH_3COCH_3)
  - Recognized biomarker for diabetes

ICL based Quartz-Enhanced Photoacoustic Gas Sensor



R. Lewicki, G. Wysocki, A.A. Kosterev, F. K. Tittel, QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 µm", submitted to Optics Express, April 2007

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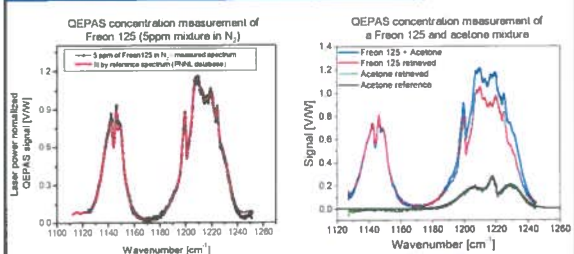
Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at λ = 8.4 µm



- Minimum detection limit (1σ) of ~4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW
- Wide tunability enables excellent molecular selectivity for broad band absorbers

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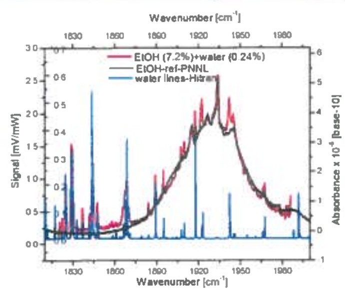
QEPAS ethanol spectrum between 1825 & 1980 cm^{-1}



Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the atmospheric water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database)

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Merits of QEPAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to environmental noise- acoustic quadrupole
- Ultrasmall sample volume (< 1 mm^3)
- Applicable over a wide range of temperatures and pressures, including atmospheric pressure
- Sensitivity is limited by the fundamental thermal TF noise: k_BT energy in the symmetric mode is directly observed
- Rugged and low cost compared to other spectroscopic techniques that require infrared detector(s)
- Sensitive to phase shift introduced by V-T relaxation processes – additional selectivity
- Potential for trace gas sensor networks

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QEPAS Performance for 11 Trace Gas Species (June'07)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	$< 4.3 \times 10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim 2.5 \times 10^{-9}$	~ 40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CH_4 (N_2)*	6057.09	950	2.9×10^{-8}	13.7	2.1
CO_2	6361.25	90	1.6×10^{-8}	26	410
CO_2 (N_2+1.5% H2O)*	4991.26	50	1.4×10^{-8}	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
C_2H_5OH **	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (Freon 125)***	1208.62	770	2.6×10^{-9}	6.6	0.003

* - Improved microresonator

** - Improved microresonator and double optical pass through ADM

*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.

NEC – noise equivalent concentration for available laser power and τ=1s time constant.

For comparison: conventional PAS 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*

* M.E. Webber et al, Appl. Opt. 42, 2119-2126 (2003)

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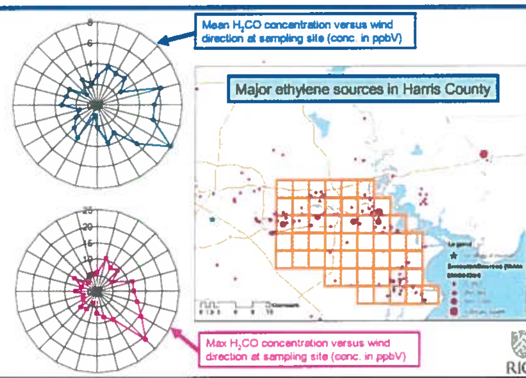
Future of Chemical Trace Gas Sensing

Existing Environmental Trace Gas Networks


- Fluxnet (pictured) (Oak Ridge National Laboratory)
  - http://www-eosdis.ornl.gov/FLUXNET
- Carbon tracker (National Oceanic and Atmospheric Administration)
  - http://www.cmdl.noaa.gov/carbontracker
- National Ecological Observatory Network (NEON) (National Science Foundation)
  - http://www.neoninc.org
- Rely on sparse data (due to cost/size of sensors) or satellite data
- Deploy with other types of sensors (e.g. wind)

H_2CO concentration (ppb) versus Wind Direction



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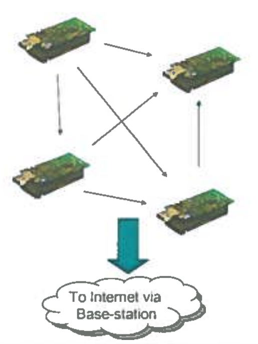
Wireless Sensor Networks for Gas Sensing



- Each point called “mote”
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

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Miniature QEPAS CO_2 sensor (λ=2μm) v2.0 boards


- 0.2W control system power consumption
- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- Projected sensitivity* to CO_2 110 ppm with 1sec. lock-in TC
- Over 10^3 improvement in sensitivity @4.2μm

*G. Wysocki, A. A. Kosterev, and F. K. Tittel "Influence of Molecular Relaxation Dynamics on Quartz-Enhanced Photoacoustic Detection of CO_2 at λ = 2 μm", Applied Physics B 85, 301-306 (2006)

Summary & Future Directions of mid-IR Sensor Technology

- **Semiconductor Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity (<10^{-4}) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 12 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5 and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Distributed sensor networks for Environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Inexpensive and sensitive sensors for industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
  - Wearable sensors for Medical & Biomedical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Hand-held sensors and sensor network technologies for Law Enforcement and Homeland Security
- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
  - Development of optically multiplexed gas sensor networks based on QEPAS

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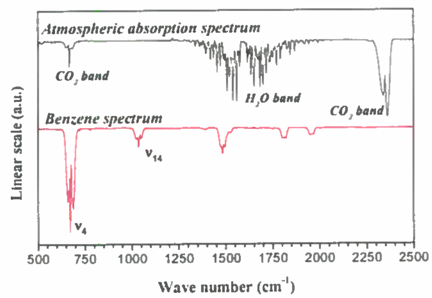
FT-IR survey absorption spectrum of benzene vapor (C_6H_6)



W.Chen, F.Cazier, F.K. Tittel and D Boucher, Appl. Optics 39, 6238, 2000

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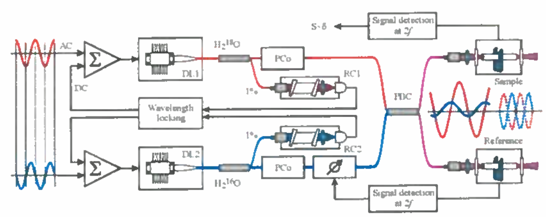
Proposed $H_2{}^{18}O$/ $H_2{}^{16}O$ Isotopic Ratiometer Scheme



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