PICARRO

Photonics & Ultrasensitive Gas Analysis

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January 2022

EPIC World Photonics Technology Summit - San Francisco - January 2022

WHO
ARE WE?

- **Leading provider of solutions** to measure greenhouse gas concentrations, trace gases and stable isotopes across **many scientific applications**, along with the **energy and utilities** markets.

- Over 45 patents owned by Picarro or exclusively licensed from Stanford University

- ISO 9001:2015 Certified Corporate Headquarters, including R & D, Engineering and Manufacturing/Operations in Santa Clara, California

- 200+ employees including 35+ STEM PhDs

- Thousands of Picarro instruments in 60+ countries world-wide

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MOLECULES MEASURED

GHG analyzers:

- Carbon Dioxide (CO_2)
- Carbon Monoxide (CO)
- Methane (CH_4)
- Nitrous Oxide (N_2O)
- Water Vapor (H_2O)
- and more...

Suitable for concentration analysis in the atmosphere. Analyzers are optimized for atmospheric concentration.

Trace gas analyzers:

- Ethane (C_2H_6)
- Ammonia (NH_3)
- Hydrogen Fluoride (HF)
- Hydrogen Chloride (HCl)
- Formaldehyde (CH_2O)
- Acetylene (C_2H_2)
- Ethylene (C_2H_4)
- Hydrogen Sulfide (H_2S)
- Hydrogen Peroxide (H_2O_2)
- Ethylene Oxide (C_2H_4O)

Suitable for trace gas detection just above nothing. "To detect the absence of a gas" these analyzers have a lower detection limit.
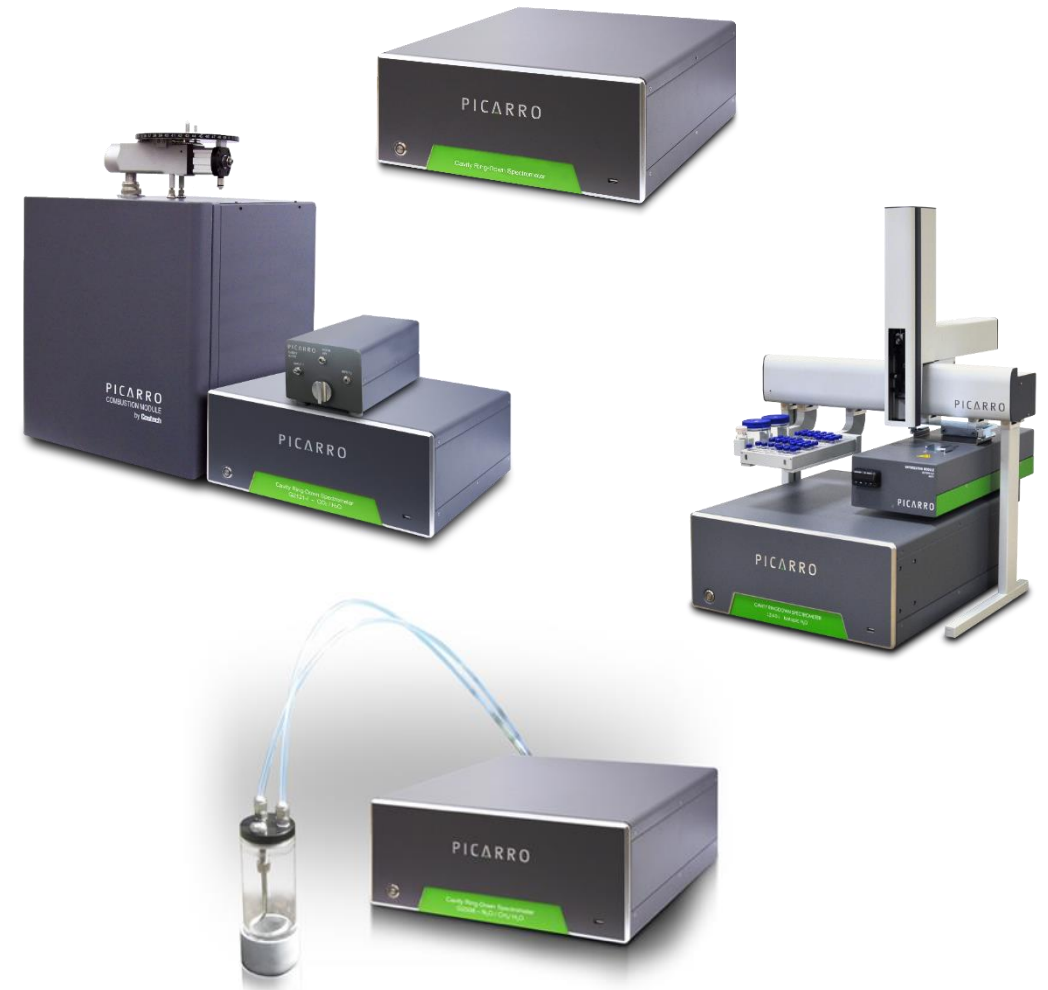
Isotope analyzers:

- $\delta^{13}C$ in high concentration CO_2
- $\delta^{13}C$ in CH_4 and C_2H_6 / CH_4
- $\delta^{13}C$ in CO_2
- $\delta^{13}C$ in CH_4
- $\delta^{13}C$ in CO_2 and CH_4
- $\delta^{18}O$ and δD in H_2O
- $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess in H_2O
- $\delta^{15}N$, $\delta^{15}Na$, $\delta^{15}Nb$ and $\delta^{18}O$ in N_2O
- O_2 concentration and $\delta^{18}O$ in O_2

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PRODUCTS SOLD

GREENHOUSE GAS AND TRACE GAS ANALYZERS

Greenhouse Gas Analyzers (concentration only)

- G2301 — CO_2, CH_4, H_2O
- G4301 — CO_2, CH_4, H_2O (portable)
- G4302 — CH_4, C_2H_6, H_2O (portable)
- G2311-*f* — CO_2, CH_4, H_2O (10Hz)
- G2401 — CO_2, CO, CH_4, H_2O
- G2401-*m* — CO_2, CO, CH_4, H_2O (flight)
- G2308 — N_2O, CH_4, H_2O
- G2508 — N_2O, CH_4, CO_2, NH_3, H_2O
- G5310 — N_2O, CO, H_2O

Peripherals for GHG Analyzers

- A0311 — 16-port Manifold, multiple inlet system
- A0701/A0702 — Recirculation Pump for closed system measurement
- A0314 — Small Sample Introduction Module (SSIM2) for discrete samples & dilution

Trace Gas Analyzers (concentration only)

- G2103 — Ammonia (NH_3)
- G2106 — Ethylene (C_2H_4)
- G2108 — Hydrogen Chloride (HCl)
- G2114 — Hydrogen Peroxide (H_2O_2)
- PI2114 — Hydrogen Peroxide (H_2O_2)
- G2203 — Acetylene (C_2H_2) and CH_4
- G2204 — Hydrogen Sulfide (H_2S) and CH_4
- G2205 — Hydrogen Fluoride (HF) and H_2O
- G2307 — Formaldehyde (CH_2O), CH_4 and H_2O
- G2910 — Ethylene Oxide (C_2H_4O), CO_2, CH_4 and H_2O

Peripherals for Trace Gas Analyzers

- A0311 — 16-port Manifold, multiple inlet system
- A0311-*s* — 16-port Manifold SilcoNert Version, multiple inlet system

ISOTOPE ANALYZERS

Carbon Isotope Analyzers

- G2131-*i* — $\delta^{13}C$ in CO_2
- G2132-*i* — $\delta^{13}C$ in CH_4
- G2201-*i* — $\delta^{13}C$ in CO_2 and CH_4
- G2121-*i* — $\delta^{13}C$ in CO_2 -> (high range for CM)
- G2210-*i* — $\delta^{13}C$ in CH_4, CH_4 and C_2H_6 concentrations

Peripherals for Carbon Isotope Analyzers

- A0311 — 16-port Manifold, multiple inlet system
- A0701/A0702 — Recirculation Pump for closed system measurement
- A0314 — Small Sample Introduction Module (SSIM2) for discrete samples & dilution
- A0201 — Combustion Module (CM) for bulk samples
- A0302 — Automate-Fx, prep device for DIC/CO_2

Nitrogen Isotope Analyzers

- G5131-*i* — Site-specific $\delta^{15}N$ and $\delta^{18}O$ in N_2O

Peripherals for Nitrogen Isotope Analyzers

- A0311 — 16-port Manifold, multiple inlet system
- A0314 — Small Sample Introduction Module (SSIM2) for discrete samples & dilution

Water Isotope Analyzers

- L2130-*i* — $\delta^{18}O$, δD in H_2O
- L2140-*i* — $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess in H_2O

Peripherals for Water Isotope Analyzers

- A0101 — Standard Delivery Module (SDM) for calibration of vapor measurements
- A0211/A0325 — High-Precision Vaporizer and Autosampler for high-precision isotope analysis of liquid water samples
- A0214 — Mirco-Combustion Module (MCM) for removal of organics from liquids
- A0213 — Induction Module (IM) for matrix-bound water extraction
- A0217 — Continuous Water Sampler (CWS) for continuous water isotope analysis

- G2207-*i* — $\delta^{18}O$ and concentrations of O_2

Note: Contact Picarro for information on other, third-party, front-end compatibility!


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AND MARKETS SERVED

- **Scientific Research:** Agronomy, Air Quality, Atmospheric Science, Ecology, Ecosystem Science, Geochemistry, Geology, Hydrology, Ocean Sciences, Soil Science

- **Emissions:** Greenhouse Gases, Industrial Emissions, Urban Emissions

- **Energy:** Natural Gas Leak Detection, Upstream Emissions and O&G Production

- **Food, Chemicals & Pharma:** Adulteration, Packaging, Supply Chain Integrity, Cleanroom Monitoring
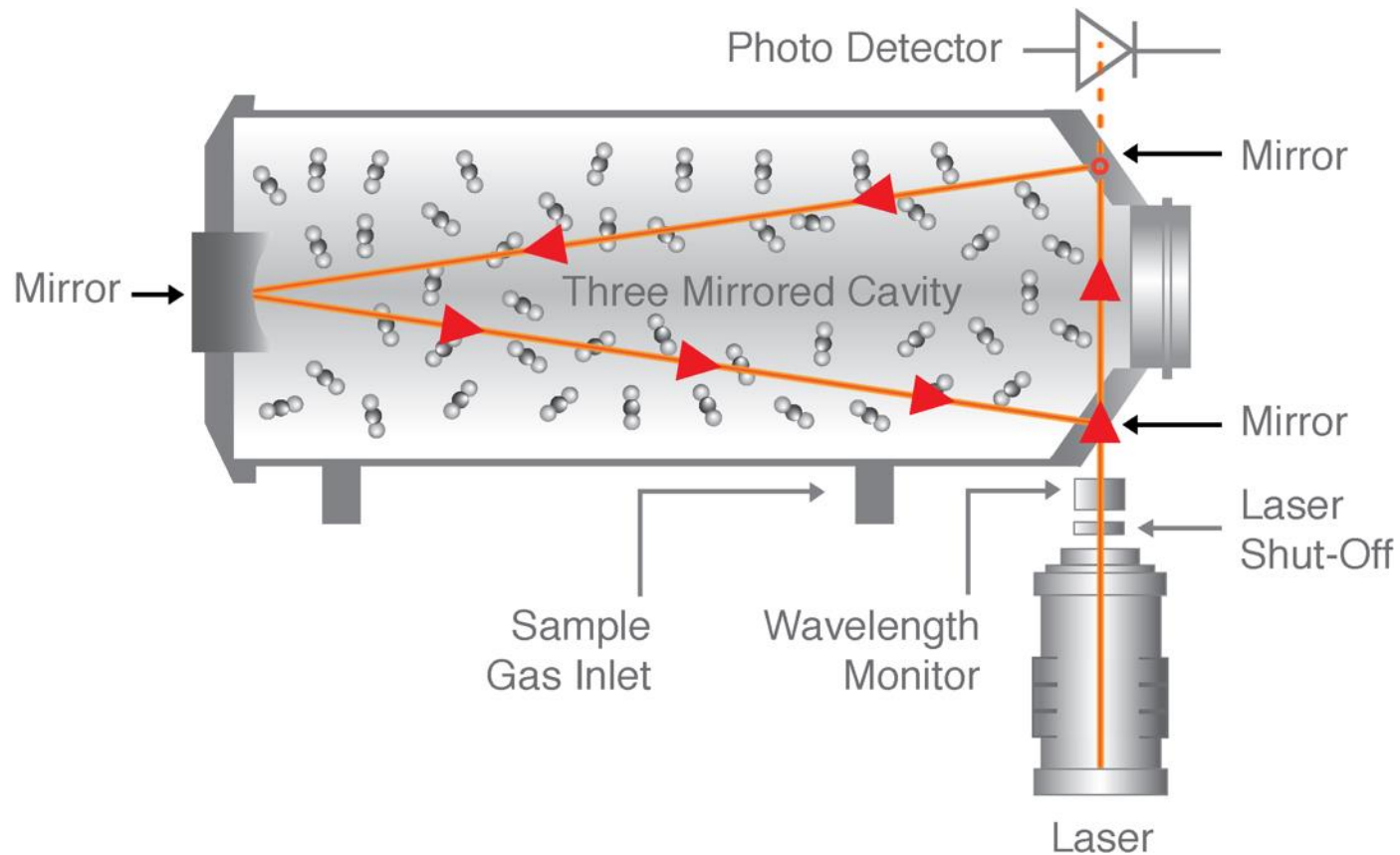
AIR

WATER

SOIL

PICARRO
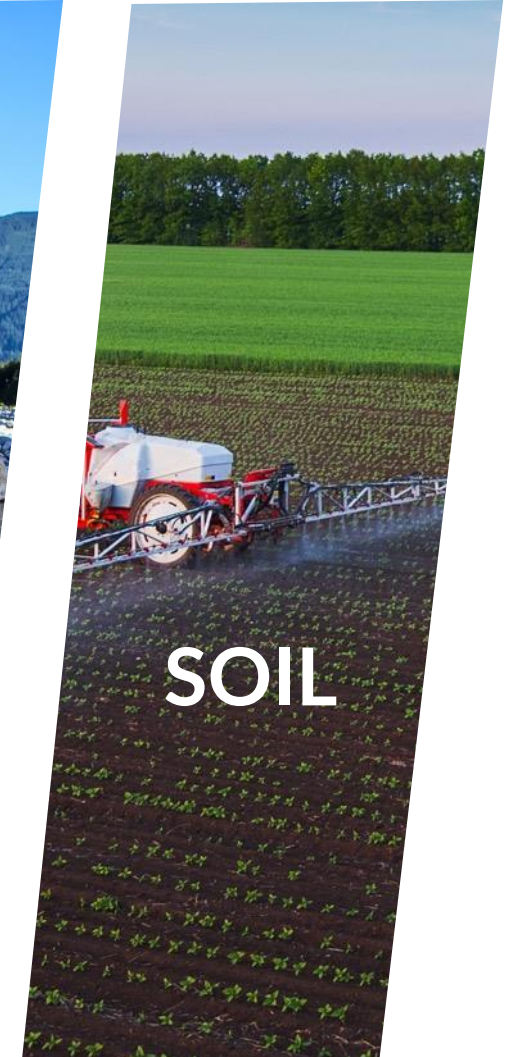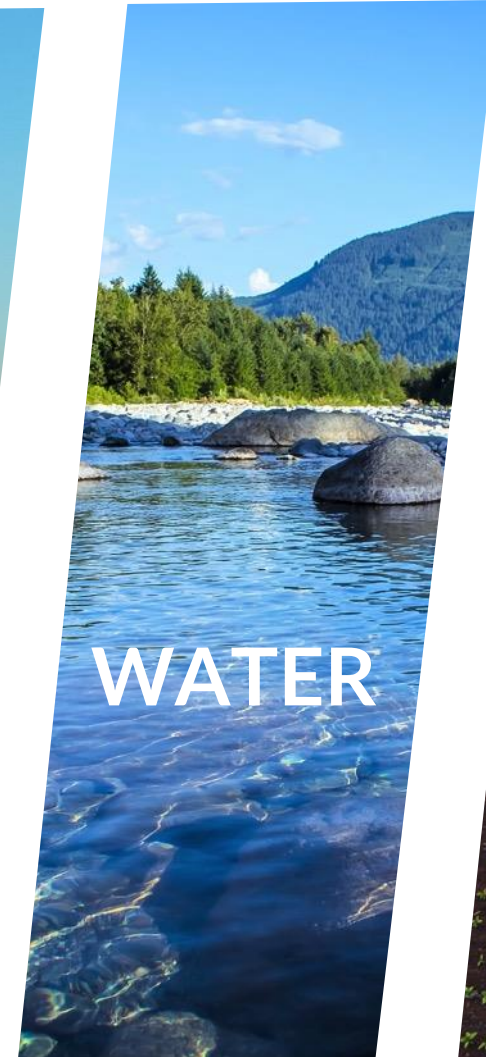
DEPLOYED ACROSS THE GLOBE, IN ANY SITUATION
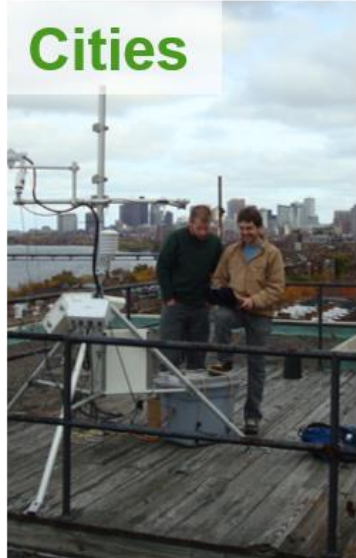
Technology Platform

Cavity Ring-Down Spectroscopy

EPIC World Photonics Technology Summit - San Francisco - January 2022

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CRDS: TIME, NOT ABSORBANCE

- CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration of (and sometimes isotopes of) H_2O, CO_2, CH_4, N_2O, CH_2O, NH_3, etc.

- Measure decay rate, rather than absolute absorbance

- Small 3-mirrored cavity ~ 35 cc

- Long effective path-length (> 10 km)

- Time-based measurement

- Laser is switched on and off, and scanned across wavelengths

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OPTICAL SPECTROSCOPY – MOLECULES IN MOTION
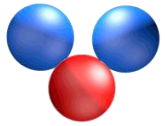
Symmetrical stretching
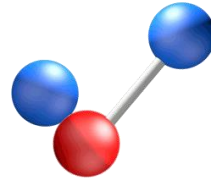
Antisymmetrical stretching
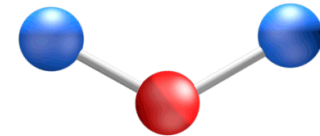
Scissoring
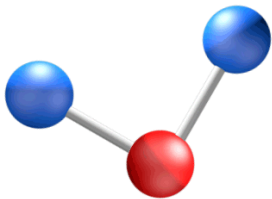
Rocking

Wagging

Twisting

PICARRO
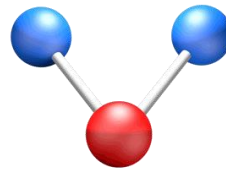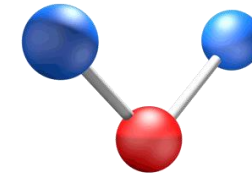
INCREASING CONCENTRATIONS FASTER RING-DOWN

Absorbing species follow Beer-Lambert Law

No gas molecules in cavity
(or absorbing at measuring
frequency)
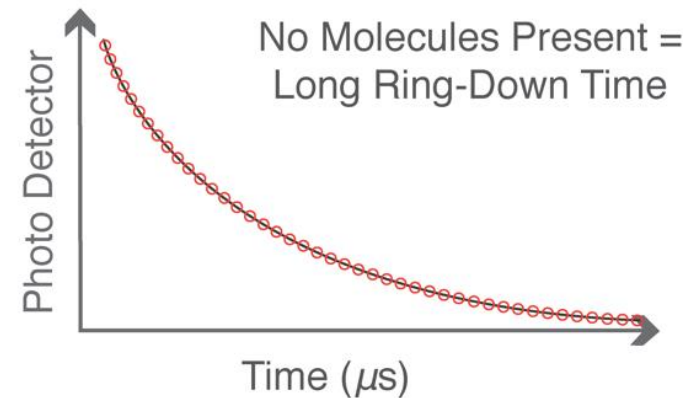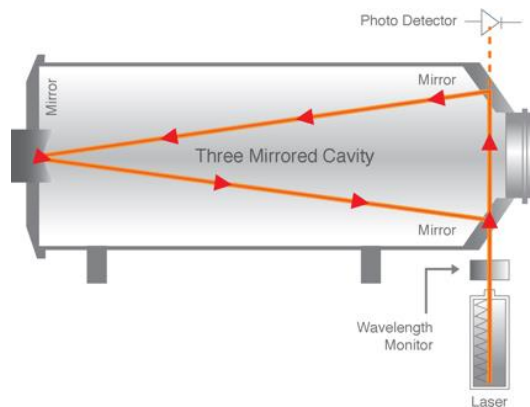
Gas molecules in cavity
(gas absorbing at
measuring frequency)
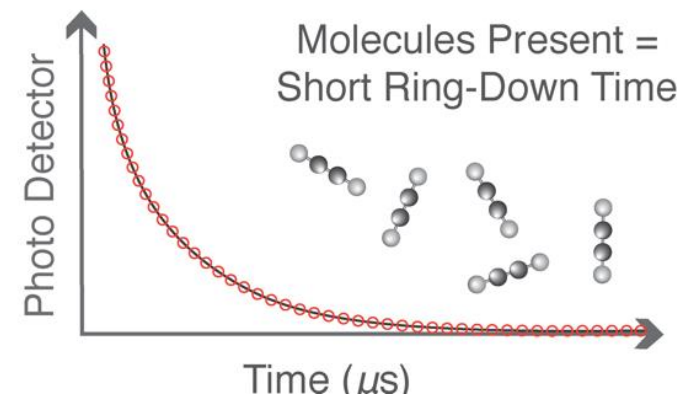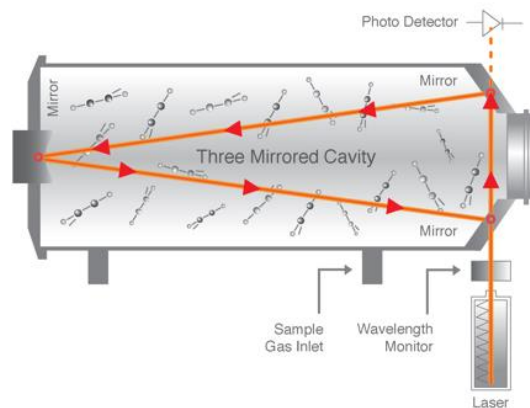
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ENABLING SCIENCE THROUGH CRDS

Carbon Isotopes

GHG Concentrations

Water Isotopes

Nitrogen & Oxygen Isotopes

Trace Gases

Flight Measurements

Soil Gas Flux

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THE FIVE S'S OF PICARRO CRDS

Selectivity

Stability

Speed

Sensitivity

Simplicity

Cavity Ring-Down Spectrometer

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GENERATING STABLE SPECTROGRAMS

1. A high-quality **absorption measurement**

   • CRDS delivers a precise and accurate measurement of the optical loss

2. A clean stable **frequency axis**

   • An accurate and precise tool for determining the laser wavelength

3. Precise **temperature control**

   • Engineered control loops

4. Precise **pressure control**

   • Engineered control loops

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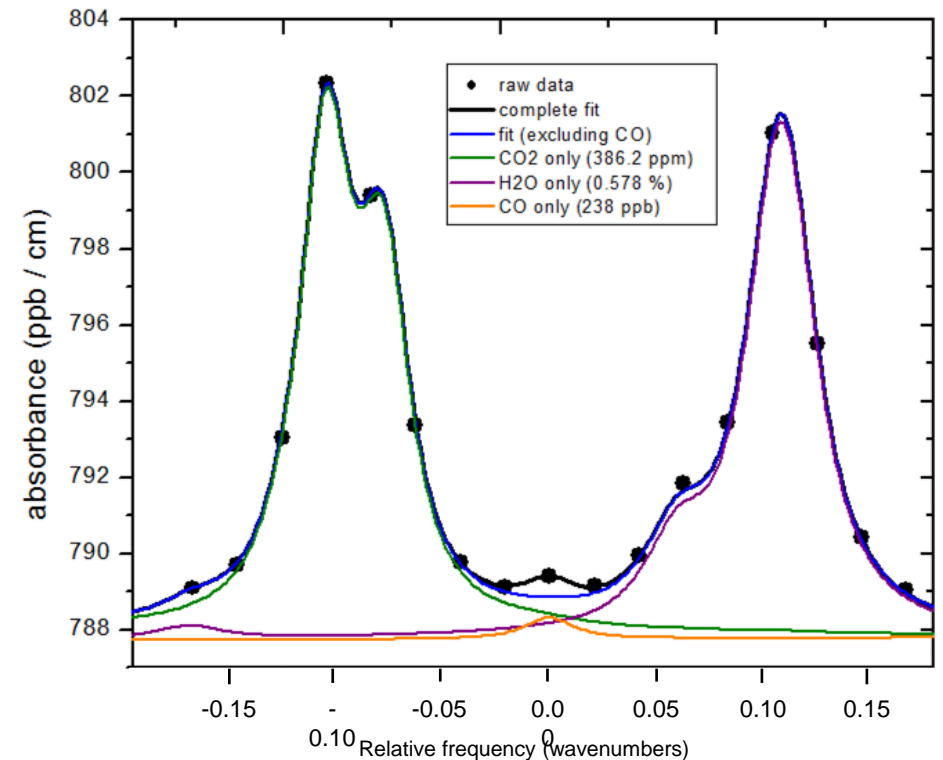
MAJOR CRDS PHOTONICS COMPONENTS

DFB-lasers

Fiber collimators
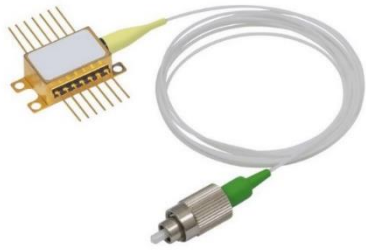
Semiconductor Optical Amplifiers (SOA) / Shatters
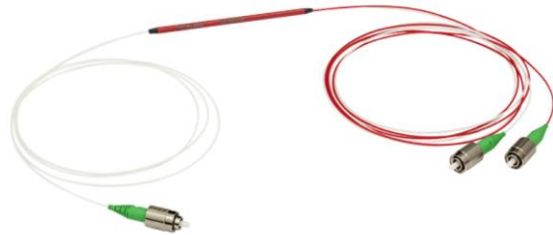
Wavelength Division Multiplexers

Photonics is the physical science and application of light generation, detection, and manipulation through emission, transmission, modulation, signal processing, switching, amplification, and sensing.
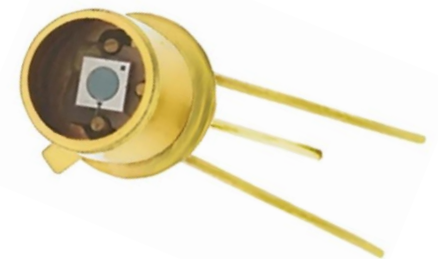
https://en.wikipedia.org/wiki/Photonics

Isolators

Optical switch
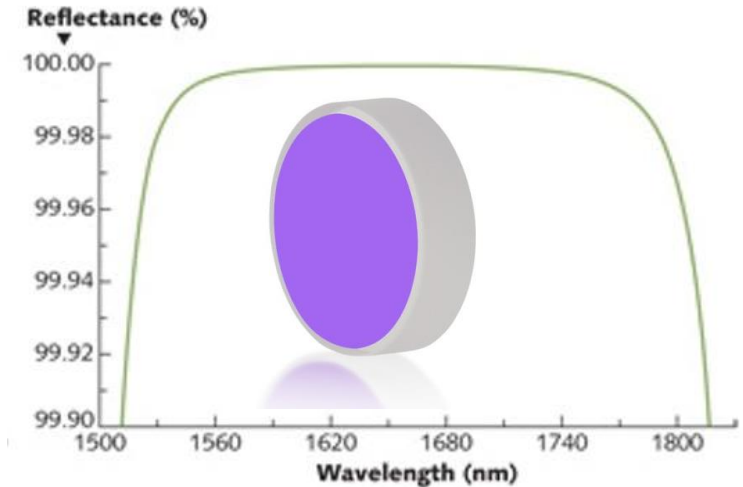
Broadband high-reflectivity mirrors

Photodiodes

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FULL LIST OF THE MOLECULES HAVING RESOLVED VIBRATION-ROTATION SPECTRA

H_2O	Water	OCS	Carbonyl Sulfide	CH_3OH	Methanol
CO_2	Carbon Dioxide	H_2CO	Formaldehyde	CH_3Br	Methyl Bromide
O_3	Ozone	$HOCl$	Hypochlorous Acid	CH_3CN	Acetonitrile
N_2O	Nitrogen oxide	N_2	Nitrogen	CF_4	PFC-14
CO	Carbon Monoxide	HCN	Hydrogen Cyanide	C_4H_2	Diacetylene
CH_4	Methane	CH_3Cl	Methyl Chloride	HC_3N	Cyanoacetylene
O_2	Oxygen	H_2O_2	Hydrogen Peroxide	H_2	Hydrogen
NO	Nitric Oxide	C_2H_2	Acetylene	CS	Carbon Monosulfide
SO_2	Sulfur Dioxide	C_2H_6	Ethane	SO_3	Sulfur trioxide
NO_2	Nitrogen Dioxide	PH_3	Phosphine	C_2N_2	Cyanogen
NH_3	Ammonia	COF_2	Carbonyl Fluoride	$COCl_2$	Phosgene
HNO_3	Nitric Acid	SF_6	Sulfur Hexafluoride	SO	Sulfur Monoxide
HF	Hydrogen Fluoride	H_2S	Hydrogen Sulfide	CH_3F	Methyl fluoride
HCl	Hydrogen Chloride	$HCOOH$	Formic Acid	GeH_4	Germane
HBr	Hydrogen Bromide	$ClONO_2$	Chlorine Nitrate	CS_2	Carbon disulfide
HI	Hydrogen Iodide	$HOBr$	Hypobromous Acid	CH_3I	Methyl iodide
ClO	Chlorine Monoxide	C_2H_4	Ethylene	NF_3	Nitrogen trifluoride

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FROM DFB LASERS TO TUNABLE LASERS

Thousands of compounds in the gas phase have broad unresolved spectra

https://agu.confex.com/agu/fm21/meetingapp.cgi/Paper/969594

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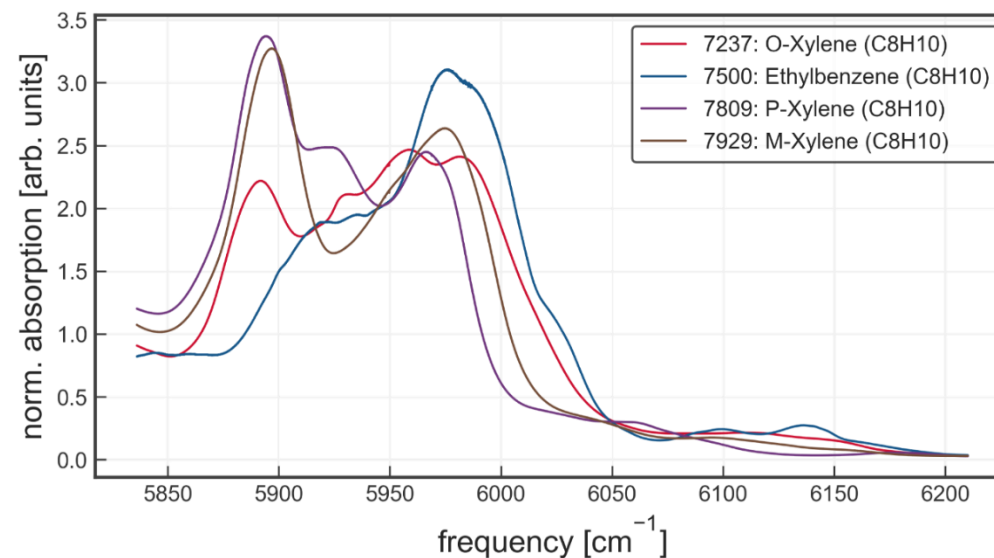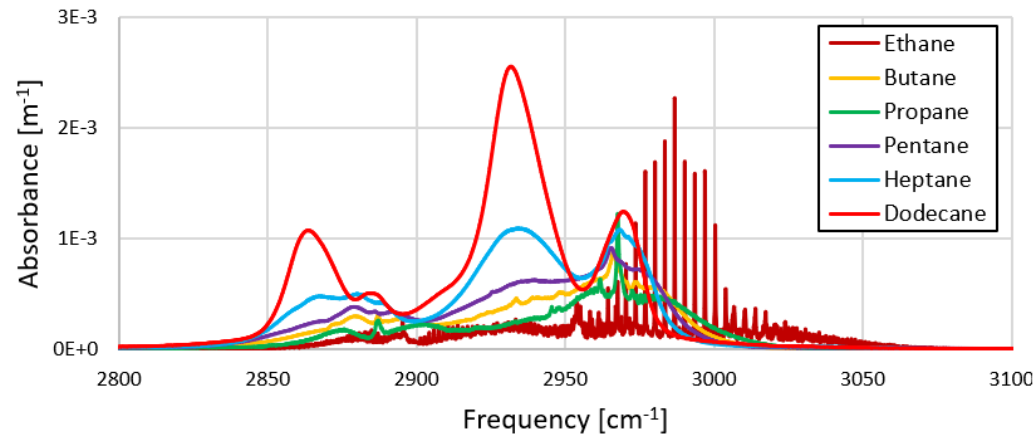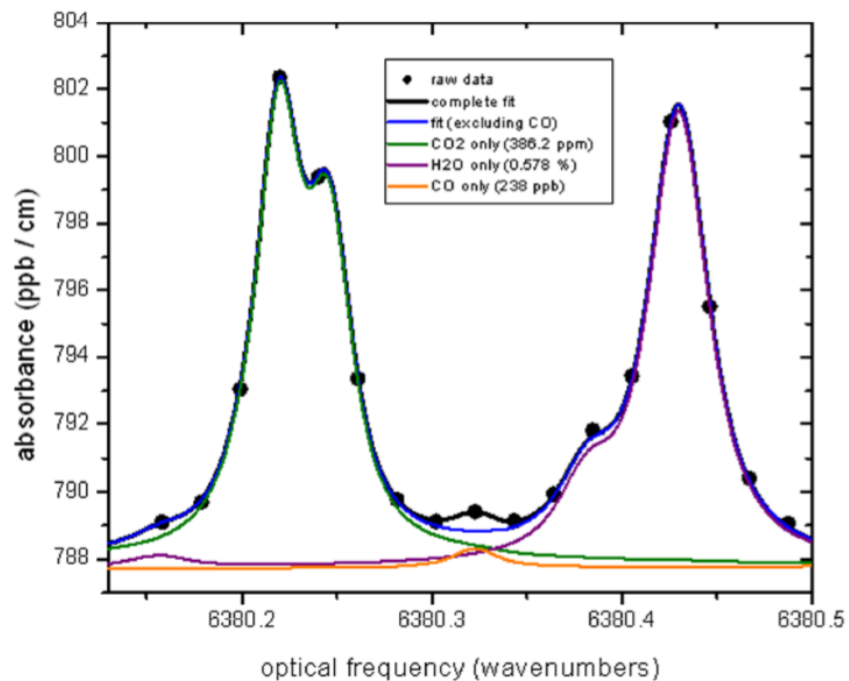
WIDELY & FAST TUNABLE LASERS

MG-Y (Modulated Grating Y-branch) laser
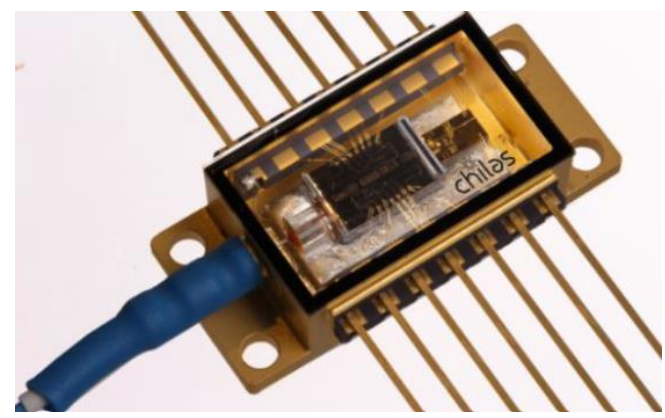
Digital Supermode (DS)–DBR laser

Our wishes:
- *Different spectral ranges (including Mid-IR)*
- *Wide tuning ranges*
- *Fast random-access tuning*
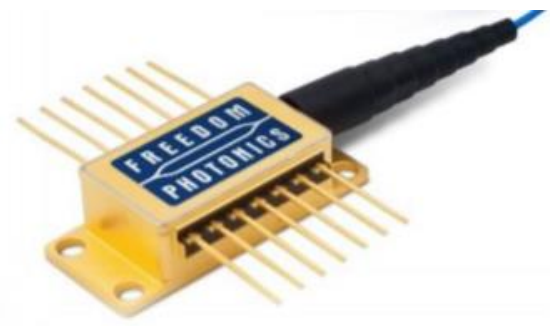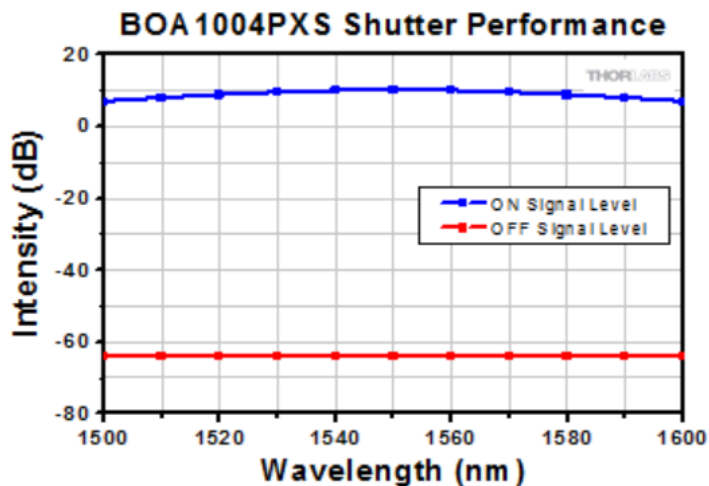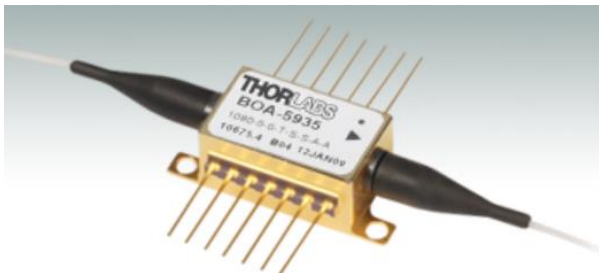- *Narrow linewidth*
- *Integrated Electronics*

Distributed Amplification Chirped Sampled Grating Distributed Reflector (DA-CSG-DR) laser

Hybrid Integrated Semiconductor Laser

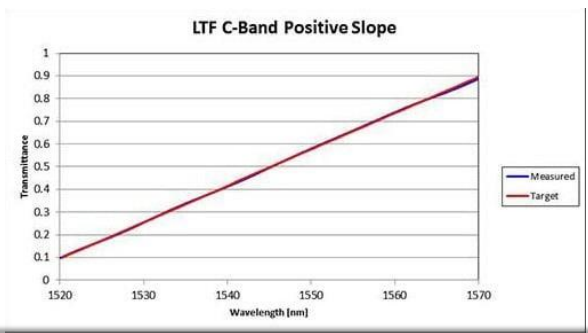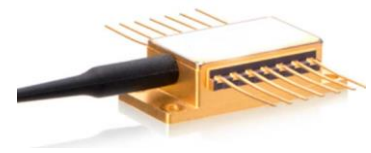*Sampled Grating Distributed Bragg Reflector (SG-DBR) laser*

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HIGH-SPEED OPTICAL SHUTTER / SOA & ABSOLUTE WAVELENGTH METER

ABSOLUTE WAVELENGTH METER

Our wishes:
- *Off-State isolation >100 dB*
- *Different spectral ranges*
- *High output power*

Our wishes:
- *Precision < 1 MHz in 100-500 nm spectral range*
- *Fast (~100 kHz) measurements to provide a feedback to a laser driver*

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HIGH REFLECTIVITY MIRRORS

R. Lalezari , N. Anderson. OPTICS FABRICATION: High-performance mirrors excel for intracavity applications. Laser Focus World. Jan. 31, 2012
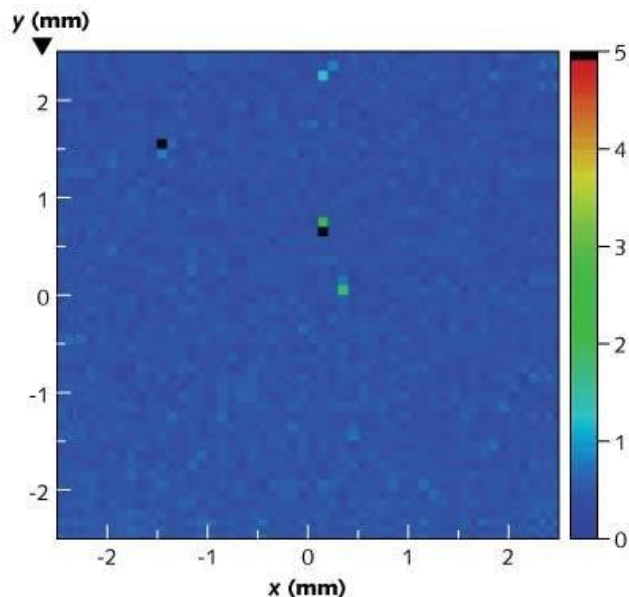
A photothermal common-path interferometry mapping of the surface of a high reflectivity dielectric mirror reveals absorption "hot spots." Here, only four regions of the mirror were found to have localized absorption losses greater than 1.5 ppm.

CHARACTERIZATION OF ADVANCED LIGO CORE OPTICS
G. Billingsley, H. Yamamoto, and L. Zhang
LIGO Laboratory
California Institute of Technology
Pasadena, California, USA.
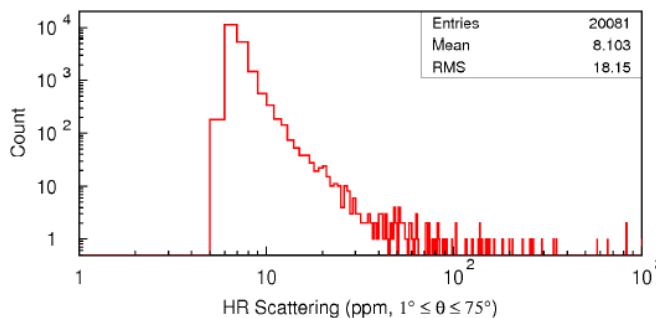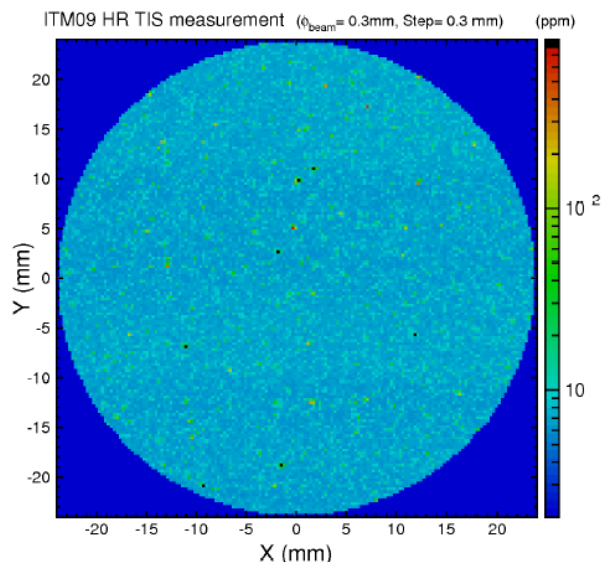
Our wishes:
- *Low scattering (< 1ppm)*
- *Low absorption (Mid-IR)*
- *High HR surface homogeneity*

Crystalline Mirror Solutions: Semiconductor Supermirrors
Optical losses on par-with with the best IBS coatings
• absorption < 1 ppm via PCI in the NIR, scatter loss < 3 ppm
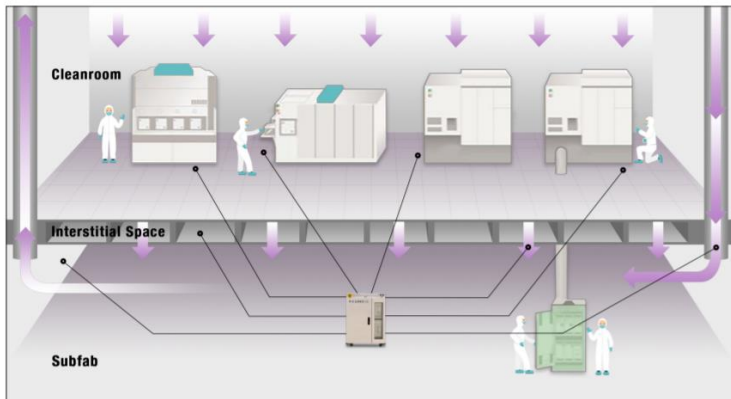• cavity finesse > 600,000 (R > 99.9995%) measured at 1550 nm

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FROM NIR TO MID-IR

BTEX, 1 ppm, 25 C, 1 Atm
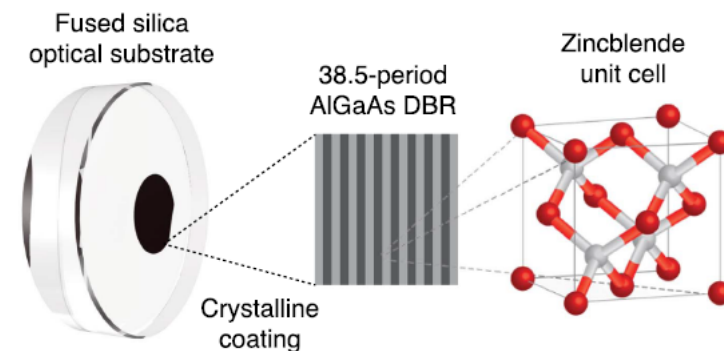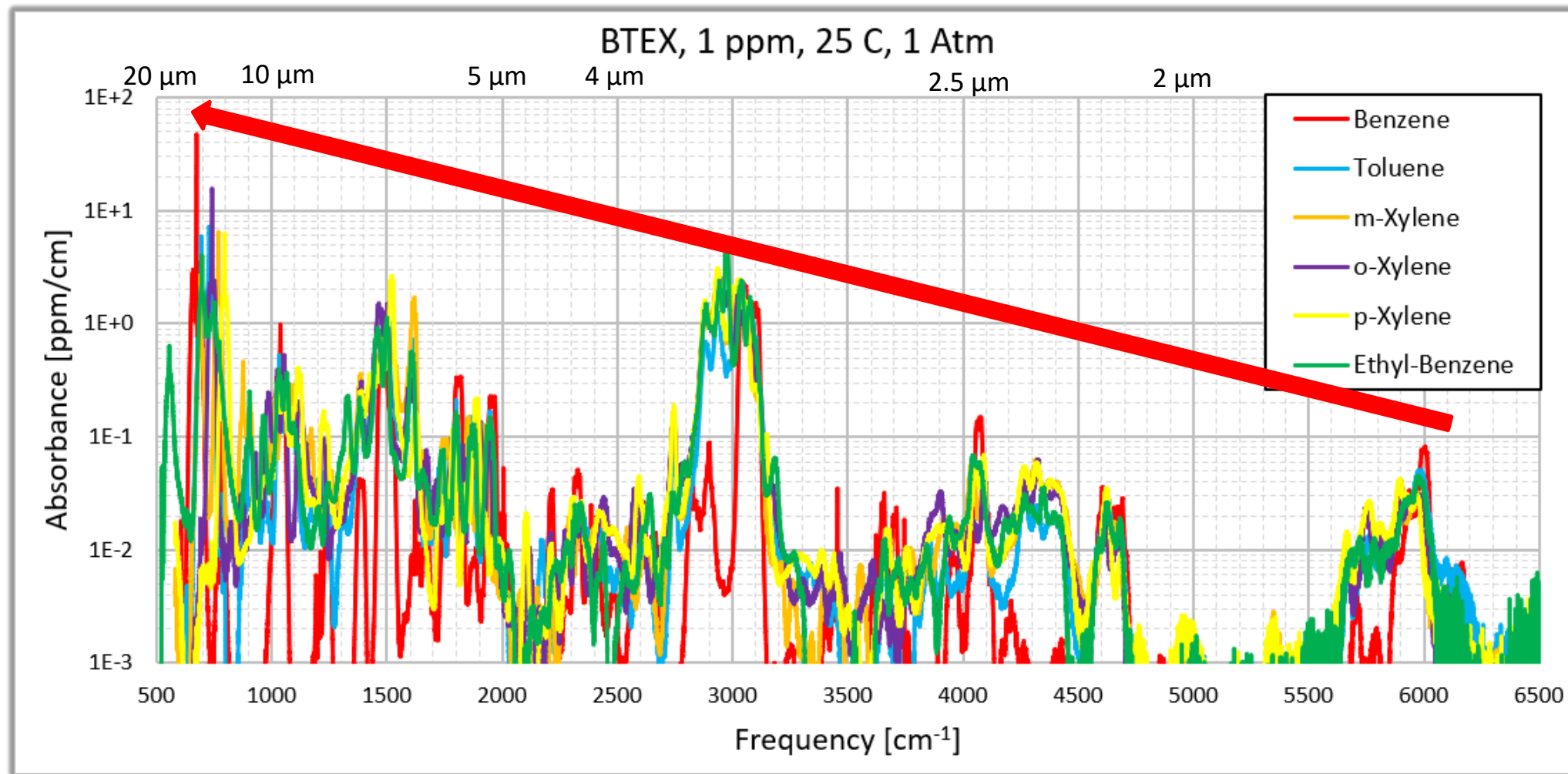
MARKETS

Multi-port Sampling System Setup for Fab AMC Monitoring

Industrial Processes

Disease biomarker detection

Exhaled Breath

Air pollution
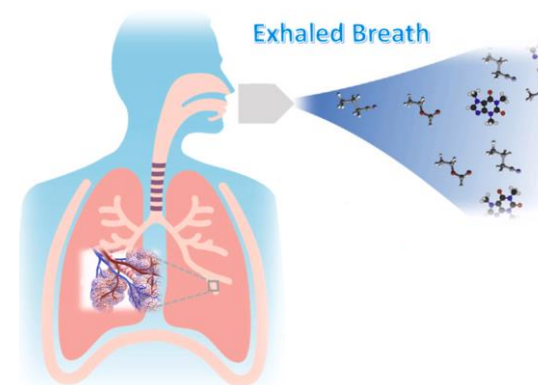
Biotech manufacturing facilities

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