IQCLWS 2008

Liquid Sensing with QCLs: Toward On-Chip MIR Sensor Technology

Boris Mizaikoff

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Monte Verita, Switzerland, September 18, 2008

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Research Activities at Georgia Tech and Univ. Ulm

Applied Sensors Laboratory and Inst. for Analytical and Bioanalytical Chemistry

Chemical Sensors and Spectroscopy

→ Infrared sensor technology
→ Sensing in harsh environments
→ QCL based IR sensors
→ Biomimetic receptors & membranes
→ Chemometrics

Bioanalytics

→ Multifunctional scanning nanoprobes
→ FIB based nanofabrication
→ Biosensors for clinical applications
→ DNA sensors
→ In-vivo IR sensors

Georgia Tech ← **New in 2008** → ulm university universität uulm

B. Mizaikoff, Anal. Chem., 75, 258A (2003); M. Kraft, et al., Appl. Spectrosc, 57, 591 (2003); A. Kueng, et al., Angew. Chem., 42, 3237, (2003); G. Dobbs, et al., Appl. Spectrosc., 60, 573 (2006)

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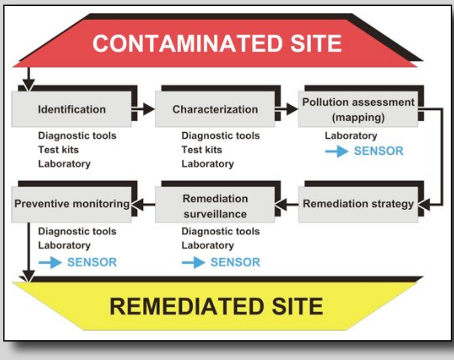
Quo Vadis Sensor Technoogy?

Toward more selectivity and sensitivity … and of course smaller and cheaper!

Given the usual complexity of the sample matrix (liquid and gas phase), quantitative in-situ/on-site analysis/sensing with molecular specificity at trace levels remain key issues.



→ Robust sensor technology
→ Sensing in harsh environments (e.g., deep sea, process analysis, nuclear, etc.)
→ Inherent molecular selectivity or (bio)recognition chemistry
→ Multicomponent analysis (usually requires chemometrics)
→ Continuous operation/monitoring in field, clinics, processes, etc.

G. Holst, B. Mizaikoff; Optical Fiber Sensors for Environmental Applications, in Handbook of Fiber Optic Sensing Technology, Wiley, 729 (2002)

How much has been done?

Quick search on SciFinder …

Keyword: quantum cascade laser

→ 1975 references

Refine: gas

→ approx. 305 references

gas + sensor

→ approx. 130 references

Refine: liquid

→ approx. 73 references

liquid + sensor

→ approx. 20 references (minus several reviews)

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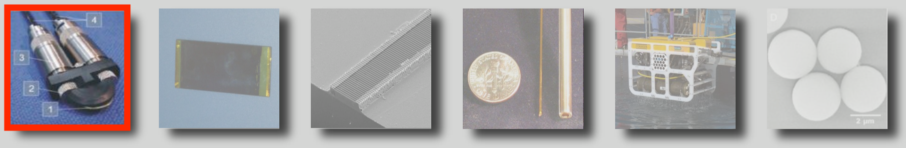
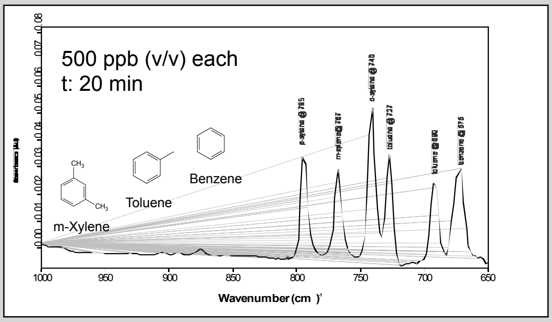
Example …

BTX monitoring with chemical IR evanescent field sensors



Collaboration: ExxonMobil



BTX in groundwater

→ Enrichment into E/Pco
→ Extracted calibrations (5 repetitions each)
→ LODs < 100 µg/L
→ Continuous monitoring possible (o-xylene in pond water)

M. Karlowatz, et al., Anal. Chem., 76, 2643-2648 (2004)

Electromagnetic Spectrum

Why mid-infrared? Unique and exquisite inherent molecular selectivity!

Mid Infrared

→ **Advantages**
+ fundamental vibrations
+ absorption cross-section
+ fingerprint region
+ inherent molec. selectivity

→ **Disadvantages**
- exotic fiber materials
- fiber length <10 m
- probe multiplexing
- water absorption

UV/Vis - Near Infrared

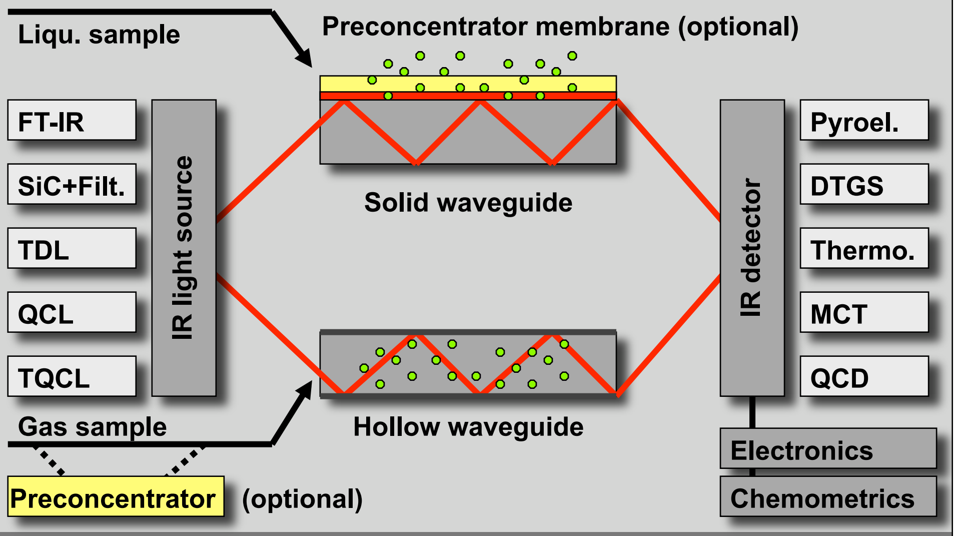
→ **Advantages**
+ fiber materials
+ fiber length >100 m
+ probe multiplexing

→ **Disadvantages**
- UV/Vis: broad electronic transitions in liqu.
- NIR: overtone vibrations
- overlapping spectral features
- needs chemometrics

B. Mizaikoff, Water Sci. Technol., 47, 35 (2003)

Infrared Sensor Technology

IR Device Schematics



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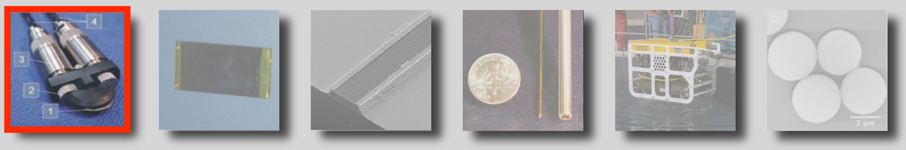
BTX monitoring with chemical IR evanescent field sensors



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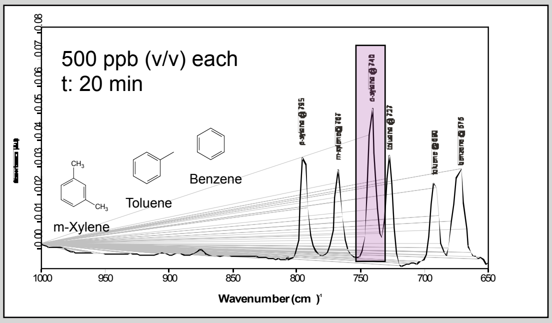

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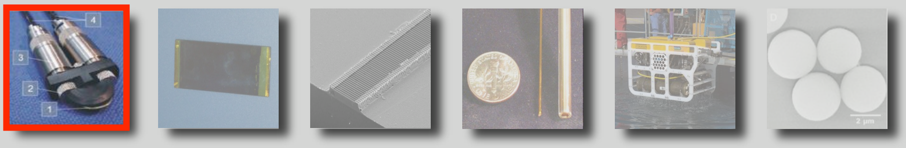

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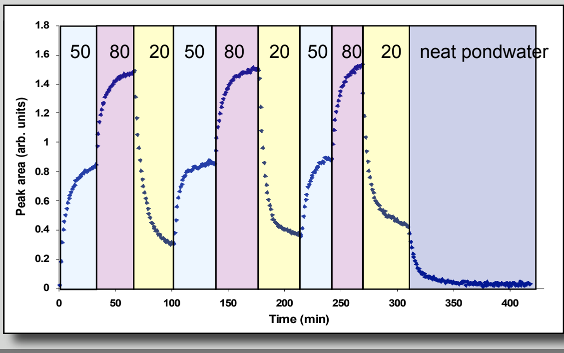

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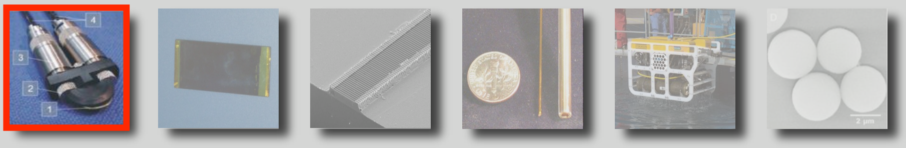

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Table 1: Overview on the most common spectroscopic measurement approaches for BTX determination in water.

Reference		38	16	19	21	48	36
Method	FTIR-ATR	FTIR-ATR	FTIR transmission	UV transmission	UV derivative spectroscopy	Photo-acoustic	SPME-NIR
SPME-matrix	EP/Co	PIB	Parafilm™	PDMS	none	none	PDMS
Simultaneous detection	yes	no*	no*	no*	yes	no*	no*
Time per measurement**	20 min	20 min	>30 min	90 min	1 min	40 min	20 min
Benzene LOD; ppb (v/v)	45	-	160	18	+/-50	308	-
Toluene LOD; ppb (v/v)	80	292	652	5	+/-50	954	173
o-Xylene LOD; ppb (v/v)	10	-	72	4	+/-50	-	-
m-Xylene LOD; ppb (v/v)	20	-	886	-	+/-50	-	-
p-Xylene LOD; ppb (v/v)	20	-	57	3	+/-50	-	129

All LODs for single analyte determinations except FTIR-ATR

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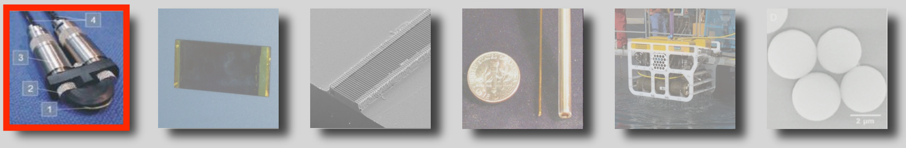

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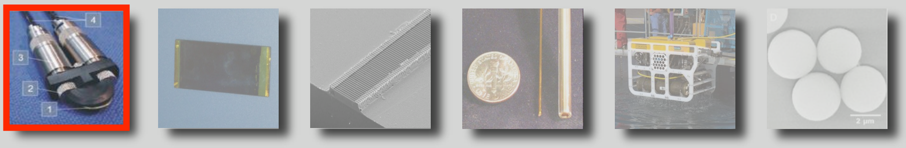
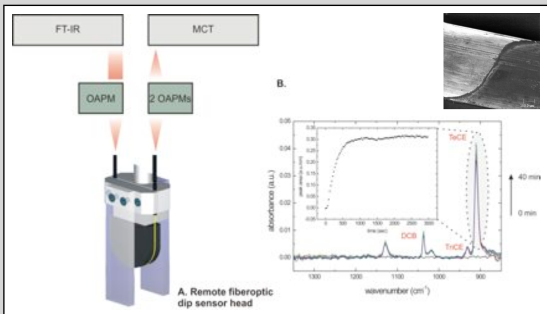
Chemical Sensors and Spectroscopy

VOC monitoring in aqueous environments with IR chemical sensors



Collaboration: A. Katzir, Tel-Aviv Univ.; R. Niessner, TUM; industrial support (e.g., ExxonMobil)



CHCs in groundwater

→ E/Pco coated AgX fiber
→ Coupled to compact FT-IR
→ Test aquifer TU Munich
→ Field deployment at landfill site (SAFIRA, Germany)
→ Rated by EPA among the most promising emerging water quality monitoring technologies
(EPA Report #EPA 542-R-03-007)

BUT: LOD needs improvement for (ultra)trace monitoring (ppb-ppt)

H. Steiner, et al., Water Sci. Technol., 47, 121-126 (2003)

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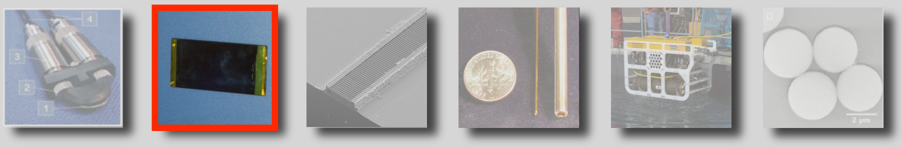
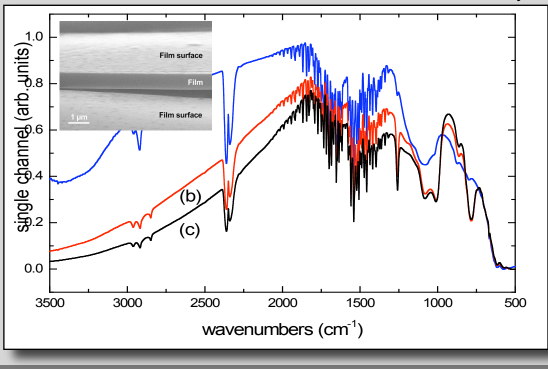
Chemical Sensors and Spectroscopy

Process monitoring: IR sensors for harsh environments



Collaboration: W. Waldhauser, Joanneum Research; R. Narayan, UNC



DLC protected waveguides

→ DLC membranes deposited with PLD-PVD @ room T
→ 30-200 nm provides 80% transmissivity
→ highly conformal pinhole-free layers
→ up to 6 months in 10 % hydrogen peroxide solution
→ simultaneous quantitative determination of acetic acid, hydrogen peroxide, peracetic acid, and peroxydisulfuric acid

M. Janotta, et al., Anal. Chem., 76, 384-391 (2004) M. Janotta, et al., Langmuir, 20, 8634 (2004) Menegazzo, et al., Langmuir, 23, 6812 (2007)

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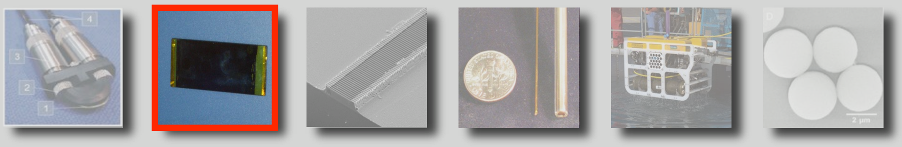

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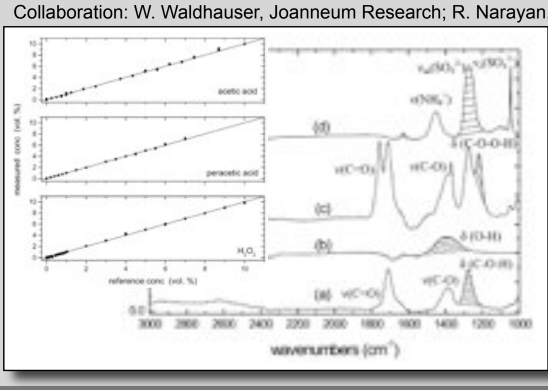

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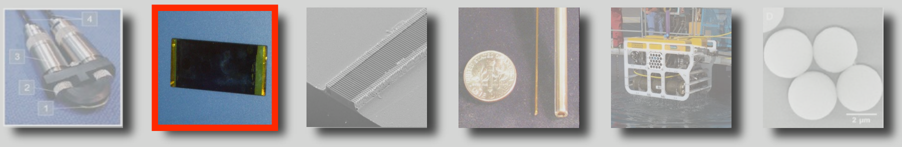

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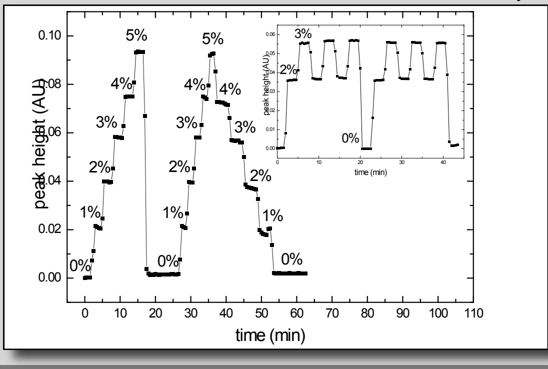

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Chemical Sensors and Spectroscopy

OPPORTUNITY & CHALLENGE

MINIATURIZATION

Macro – Micro – Nano

KEY :
Advanced Waveguide Technology

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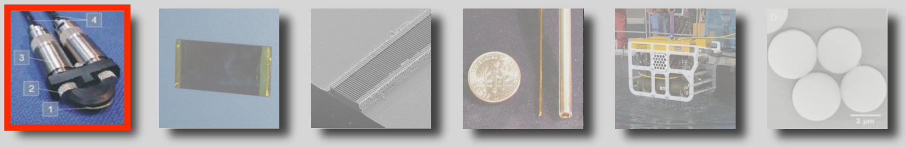
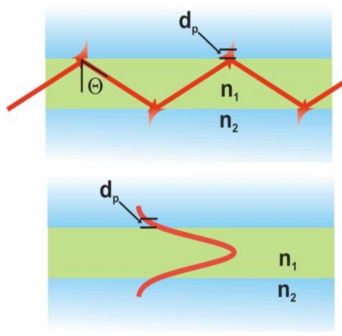
Chemical Sensors and Spectroscopy

Evanescent field sensing





Applied to opaque, highly absorbing, turbid, or biological matrices.

$$d_p = \frac{\lambda}{2\pi n_1 \cdot \sqrt{\sin^2\theta - n_{21}^2}}$$

Measurement principle:
Evanescent field absorption

→ Light is confined to waveguide
→ Analyte on top of waveguide
→ Interaction via exponentially decaying evanescent field
→ For evanescent field sensing: A = r (ε c l); r … fractional power guided outside the core
→ Penetration depth d_p and r depend on λ, θ, n_1/n_2 contrast, and the waveguide geometry
→ **Advantage in MIR:** penetration depth due to λ!

J. Fahrenfort, Spectrochim. Acta, 17, 698 (1961)
N. J. Harrick, Internal Reflectance Spectroscopy, Wiley (1967)

Sensing in Extreme Environments

Example: Petroleum industries – The need: Molecular Management

Survey & Exploration	Production & Retrieval	Transport & Storage	Refinement & Processing

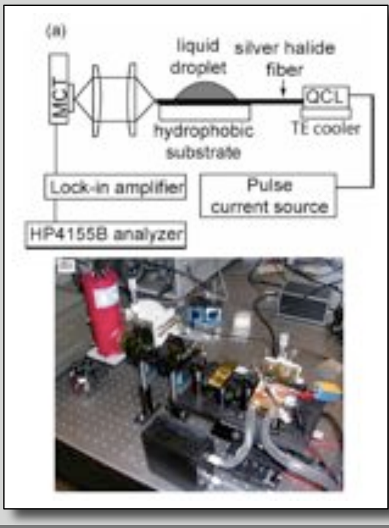
NEED:
Molecular level diagnostics & sensors

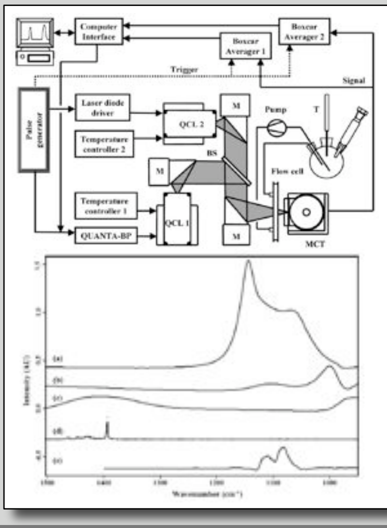
→ Characterization & analysis
→ Quality control
→ Workplace health & safety
→ Environmental health & safety
→ Process monitoring

BETTER!
in-situ, on-line, on-site

QCLs for Liquid Phase Analysis

Few examples in literature …



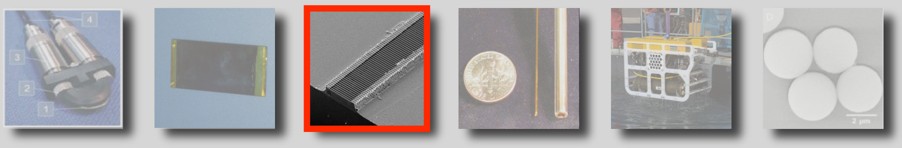


J. Z. Chen, et al.,, Opt. Expr.,13, 5953-5960 (2005)

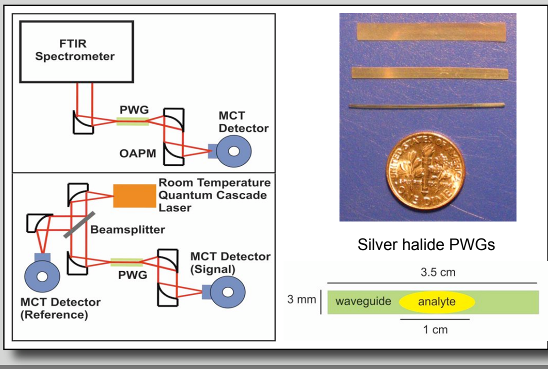
S. Schaden, et al., Appl. Spectrosc., 60, 568-571 (2006)

Chemical Sensors and Spectroscopy

Quantum cascade laser (QCL) based sensors for liquid phase trace analysis



Collaboration: A. Katzir, Tel-Aviv Univ.



Example:
QCL trace sensing in liquids

→ QCL emission at 1650 cm^{-1} overlaps with absorption
→ QCL emission is damped as urea is deposited at surface
→ trend is the same as FT-IR measurements
→ LOD = 80.7 µg (4 times FT-IR LOD !!!)

C. Charlton, et al., Anal. Chem., 77, 4398 (2005)

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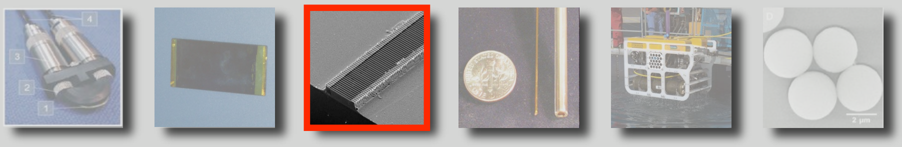

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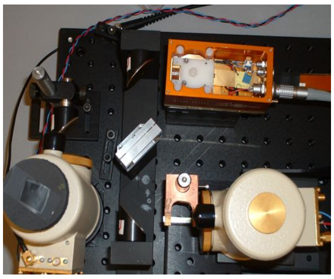

Urea (solid)
Laser s1869 ν = 1650 cm^{-1}
Pulse duration = 200 ns
Period = 25.8 µs
Temperature = 20 °C

Acetic anhydride (liquid)
Laser s1537 ν = 974 cm^{-1}
Pulse duration = 40 ns
Period = 2.64 µs
Temperature = 0 °C

First QCL evanescent field sensor with PWGs

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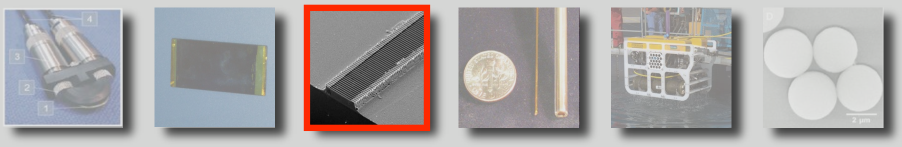
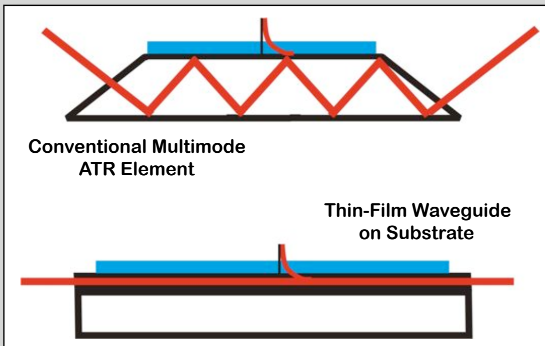


Collaboration: J. Faist, Univ. Neuchatel



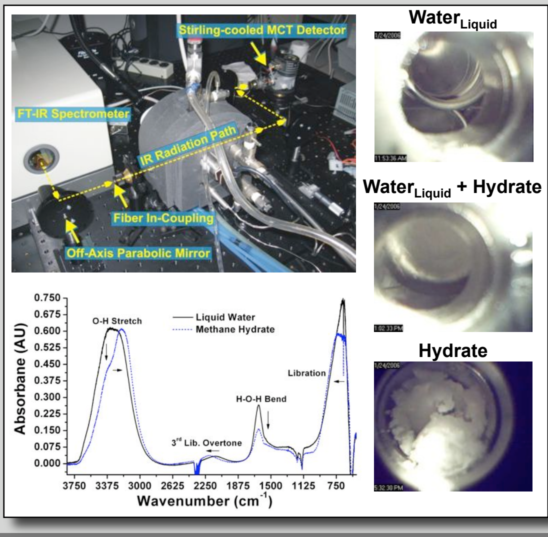
Ideal solution …

→ Thin-film mid-infrared waveguide (few microns)
→ Frequency matched to QCL
→ Well-defined evanescent field
→ Superior mode control
→ Toward the theoretical sensitivity limits of evanescent field sensing

… requires new waveguide technology!

Analysis of Gas Hydrates with IR Sensors

Gas Hydrate Monitoring in Simulated Harsh Environments with IR Sensors



Gas Hydrates in DI Water

→ Uncoated AgX fiber
→ Simulated deep-sea pressure and temperature
→ Fiber coupled to benchtop FT-IR
→ Monitoring of shifts in water absorption during phase changes
→ Stirling-cooled MCT conducive for long-term continuous monitoring

→ **Evaluated:** Methane, ethane, propane, and CO_2 gas hydrate growth dynamics continuously for up to 30 days

→ **Next step:** improved evaluation of pressure, temperature, salinity, pH, and spectral mineral effects on water absorption features

AgX … silver halide

G. T. Dobbs, Y. Luzinova, Y. Raichlin, A. Katzir, and B. Mizaikoff, manuscript in preparation (2008)

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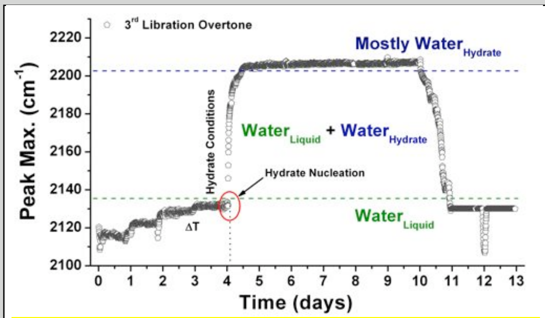
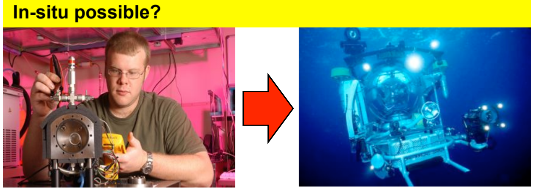


In-situ possible?



Experimental Results

→ Evaluation of peak shifts and intensity changes from multiple water absorption features enables spectroscopic monitoring of gas hydrate formation and dissociation
→ Suitable for spatio-temporal evaluation in oceanic gas hydrate ecosystems

Significance

→ **Important:** for the first time gas hydrate formation/dissociation has been spectroscopically monitored in the IR regime
→ **Potential:** gas hydrate analysis, exploration, and retrieval; gas hydrate sensing in pipelines

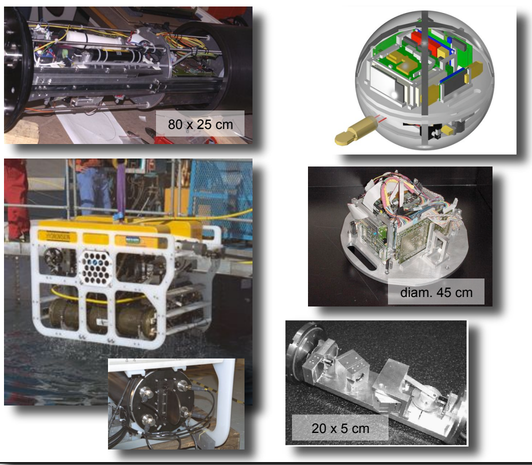
G. T. Dobbs, Y. Luzinova, Y. Raichlin, A. Katzir, and B. Mizaikoff, manuscript in preparation (2008)

Next-Generation IR Sensor Technology

IR Technology for Extreme Environments

Deep-sea FT-IR spectrometers

First generation | **Second generation**



FT-IR Based Systems

→ **The first** fully featured FT-IR spectrometers for operation in marine environments
→ TUBE IR: 1,000 m
→ SPHERE IR: 6,000 m
→ Fiberoptic or planar sensing head
→ **Alternative:** HWG sensing after membrane extraction

Significance

→ In-situ deep sea analysis of dissolved hydrocarbons (e.g. BTX), carbonates, diamantoids, gas hydrates, etc.
→ **Potential for direct in-situ IR analysis**

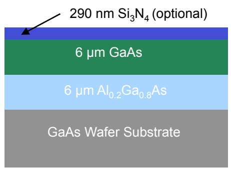
(left) TUBE FT-IR with fiberoptic sensing head (opt. for a depth of 1,000 m); (right) SPHERE FT-IR with fiberoptic or planar sensing head (opt. for a depth of 6,000 m).

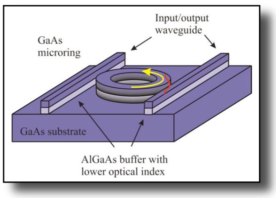
M. Kraft, et al., Appl. Spectrosc., 57, 591 (2003) G. Dobbs, et al., Appl. Spectrosc., 60, 573 (2006) T. Beyer, et al., Sens. & Act. B, 90, 319 (2003)

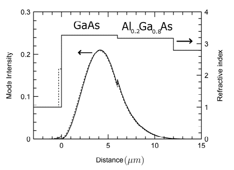
Next-Generation IR Sensor Technology

A Quantum Leap in IR Technology …

Thin-film IR waveguides | **Integrated IR resonators**







Chip-integrated IR Devices

→ **The first** thin-film mid-infrared planar waveguides (GaAs/AlGaAs)
→ Tunable to ANY frequency
→ Fabrication at a wafer scale
→ **The first** mid-IR ring resonators
→ Probably 5 years from now fully integrated on-chip IR sensing devices!

Significance

→ On-chip IR sensor technology
→ Cheap & mass-producable
→ **Potential for all in-situ, on-site, and on-line scenarios - even if you want to throw the device into the sample!**

(left) Single-mode GaAs/AlGaAs waveguides and QCL-based sensor; (right) Integrated IR resonators for monolithic on-chip integration of entire IR sensing device.

C. Charlton, et al., Anal. Chem., 78, 4224 (2006) B. Mizaikoff, et al., Patent granted (2007) B. Mizaikoff, et al., Patent filed (2008)

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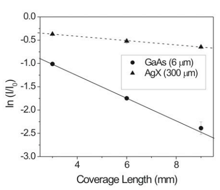
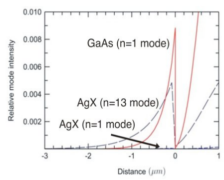
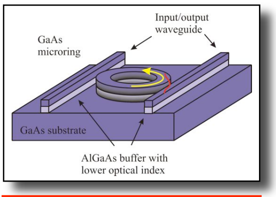


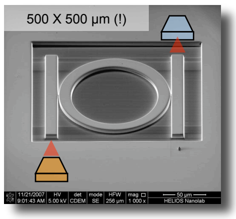
5x increase for new waveguide over AgX !



Integrated IR resonators



Chip-integrated MIR assays



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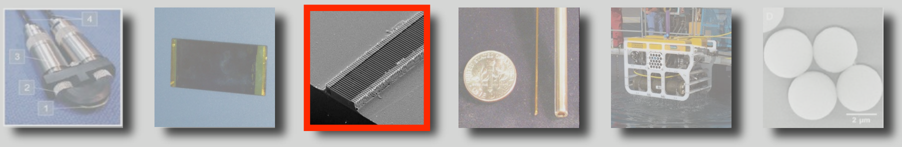
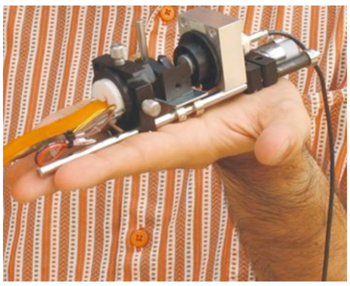
Chemical Sensors and Spectroscopy

Quantum cascade laser (QCL) based sensors for liquid phase trace analysis



Collaboration: J. Faist, Univ. Neuchatel



First handheld QCL evanescent field sensor

Results

→ Intensity of GaAs fundamental mode much higher than AgX high order mode
→ AgX fundamental and high order modes vary in evanescent intensity
→ GaAs evanescent intensity high at waveguide surface ⇒ quantitative monolayer sensing conceivable

→ **NEXT:** label free detection of bio-molecular interactions with IR (e.g. mid-infrared DNA assays); breath condensate analysis; **NIH**

C. Charlton, et al., Anal. Chem., 78, 4224 (2006)

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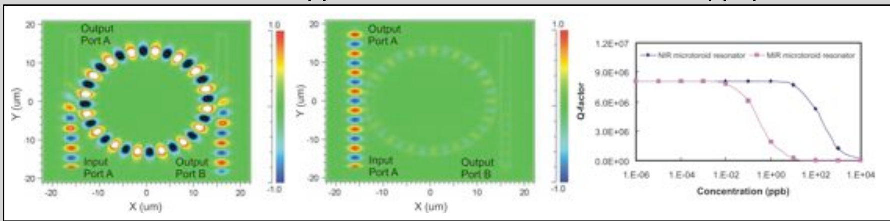
Back to Waveguide Technology

The latest findings … liquid phase sensing and assays

→ Enhanced FIB prototyping of GaAs/AlGaAs structures

→ 3-4 orders of magnitude more sensitivity (Q-factor) compared to NIR:
NIR: detection of 100 ppb toluene; MIR: detection of 10 ppt possible!

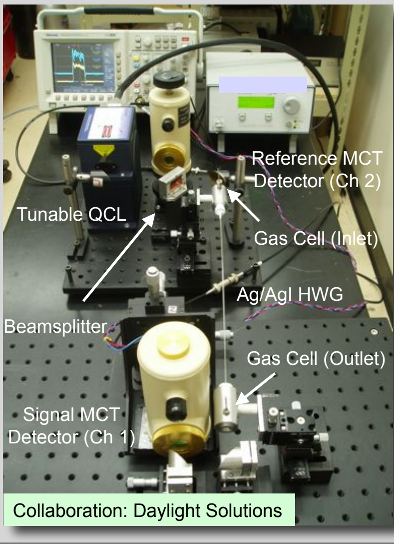


(left) TM-mode in resonance (13.6 µm); (middle) out of resonance (13.2 µm); (right) comparison Q-factor sensing MIR vs. NIR

B. Mizaikoff, et al., Patent filed (2007)   S-S. Kim. et. al., manuscript in preparation (2008)

Tunable EC-QCL - Hollow Waveguide Gas Sensor

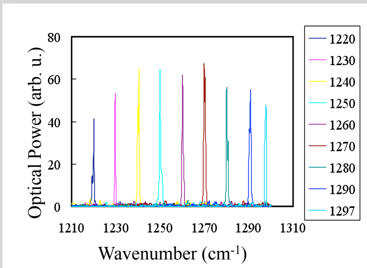
Experimental setup



→ Tuning range of QCL: 1219 cm^{-1} – 1297 cm^{-1}

→ 0.5 µs pulse width, 10 KHz frequency, 0.5 % duty cycle, 128 avg.

Next generation tunable QCL module:



C. Young. et. al., manuscript submitted (2008)

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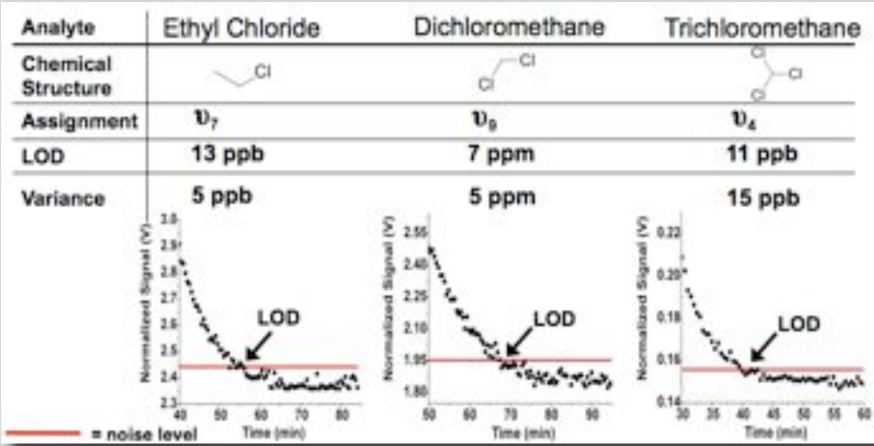
QCL Based Miniaturized IR Sensors

Latest results …



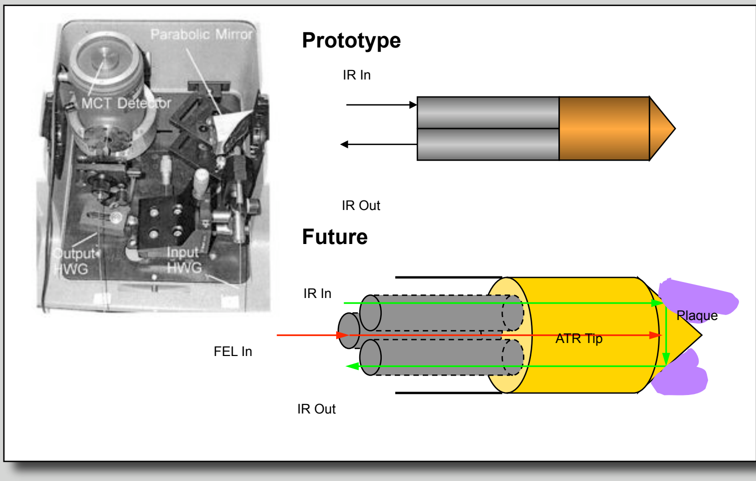
Analyte	Ethyl Chloride	Dichloromethane	Trichloromethane
Chemical Structure			
Assignment	ν_7	ν_9	ν_4
LOD	13 ppb	7 ppm	11 ppb
Variance	5 ppb	5 ppm	15 ppb

C. Young. et. al., manuscript submitted (2008)

Other projects where this will be important …

Why small is sometimes better!

Collaboration: R. Palmer, O. van Ramm, Duke Univ.



→ **FIRST** IR catheter for in-vivo atherosclerotic aorta plaque diagnosis during ablation (FEL)

L. Wang, et al., J. Biomed Optics, 12, 0240061 (2007) L. Wang, et al., Appl. Spectrosc., 60, 1121 (2006)

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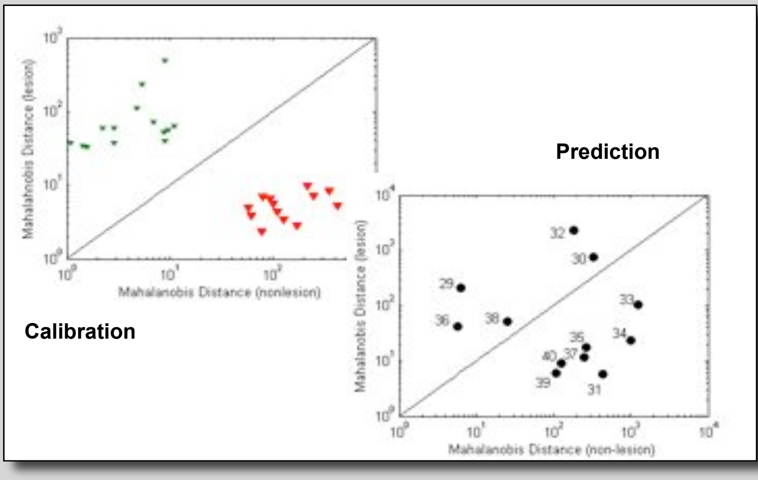

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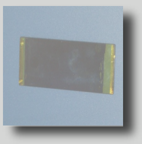
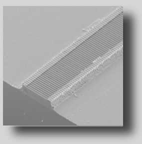
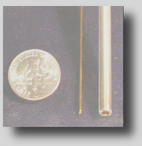
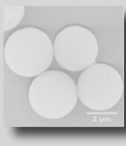
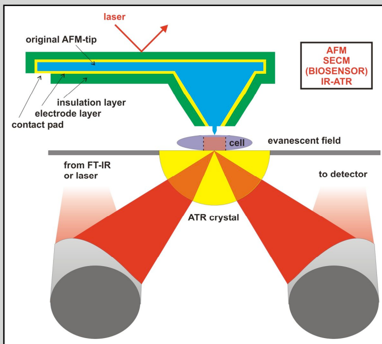
Bioanalytics

Combining evanescent field sensing with AFM





Next level of hyphenation:

topography
+
electrochemistry
+
spectroscopy

Our goal:
AFM-SECM-IR-ATR

→ Interesting tool for cellular studies
→ GOAL: determining bulk changes via IR-ATR spectroscopy correlated with topography and electrochemical imaging at biological systems
→ Current stage of development: AFM-IR-ATR for simultaneous monitoring of topographical and spectroscopic changes

BUT: LOD needs to be improved for biological applications !

M. Brucherseifer, et al., Anal. Chem., 79, 8803 (2007)

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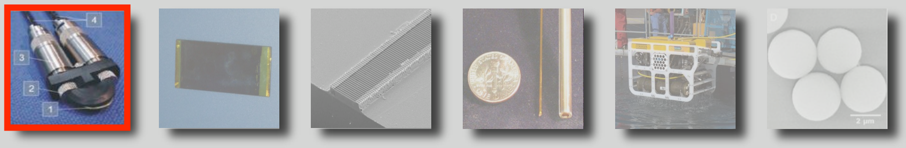

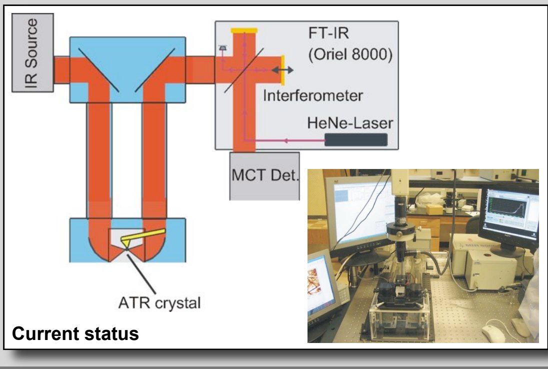

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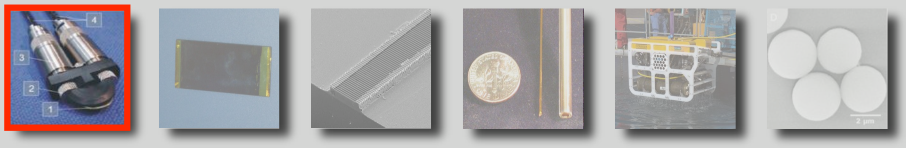

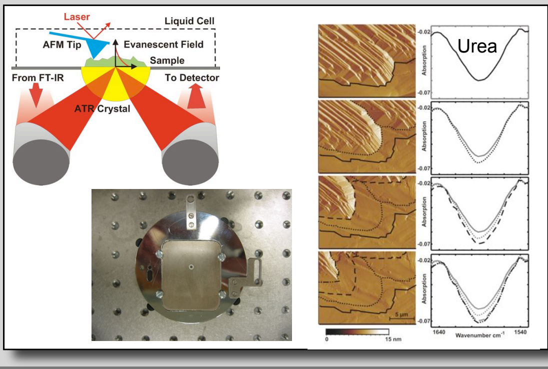

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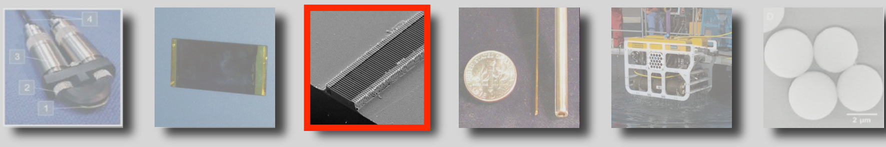

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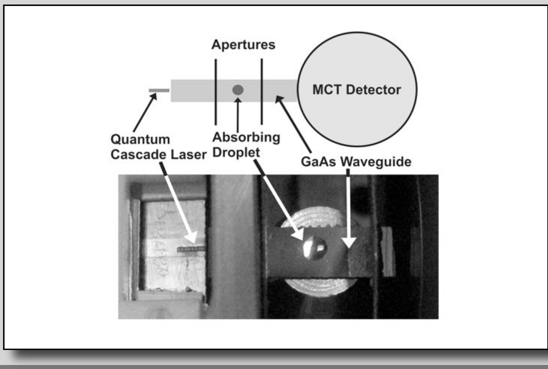


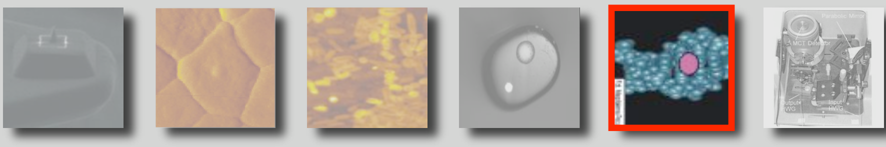
Single-mode MIR waveguides

- → **In this example:** DFB QCL @ 10.3 µm (TM00)
- → Waveguides grown by molecular beam epitaxy (MBE) on GaAs wafer substrate
- → Low loss guides enable lengths of a few centimeters with very low losses
- → QCL and MCT detector pig-tail coupled to thin-film waveguide
- → Absorbing liquid drop deposited at waveguide surface

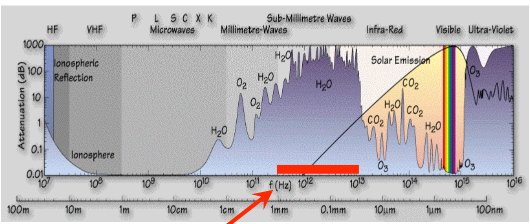
C. Charlton, et al., Anal. Chem., 78, 4224 (2006); patent granted (2008)

New Project

Label-free THz (bio)sensors



Collaboration: P. Haring, Univ. Siegen



ν = 300 GHz … 10 THz
λ = 1mm … 30µm
k = 10cm^{-1} .. 300cm^{-1}

New project: THz DNA sensing

- → Development of micro-fabricated co-axial THz nearfield emitters for bio-molecule imaging with spatial resolution < 1 µm (CMOS & FIB)
- → Integrated THz sensor chips
- → Label-free optical detection of biomolecular interactions (e.g., DNA hybridization, etc.)

(complementary to MIR efforts)

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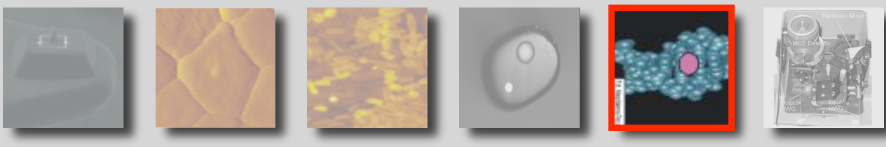

Collaboration: P. Haring, Univ. Siegen

„Biological systems are expected to have a branch of longitudinal electric modes in a frequency region between 10^{11} and 10^{12} Hz.“

H. Fröhlich J. Quant. Chem. 2, 641 (1968)

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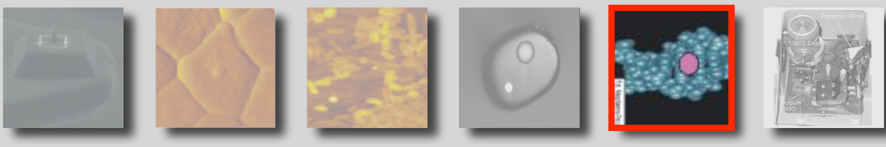
New Project

THz DNA & protein detection



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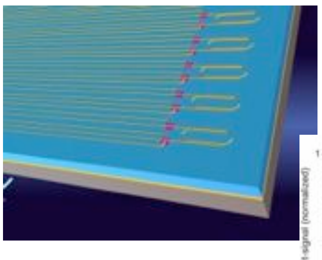

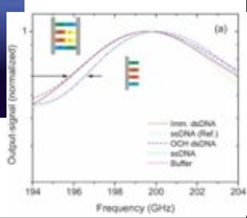

THz DNA detection scheme

New project:
THz DNA/protein sensing

→ Development of micro-fabricated co-axial THz nearfield emitters for bio-molecule imaging with spatial resolution < 1 μm (CMOS & FIB)
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H. Shin, et al., manuscript in preparation (2008)   Mizaikoff, et al., patent granted (2008)

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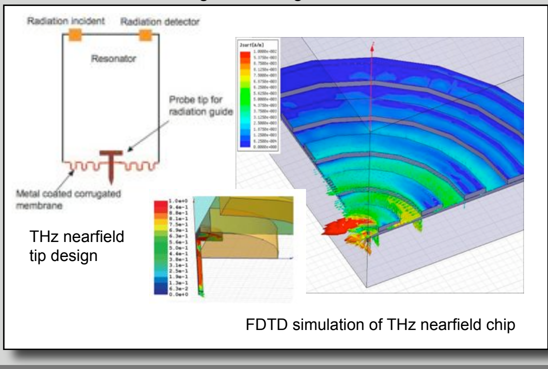

FDTD simulation of THz nearfield chip

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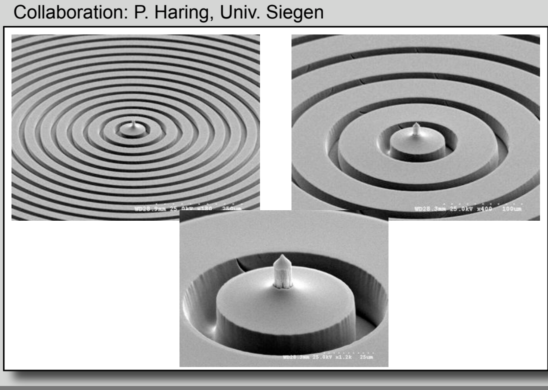

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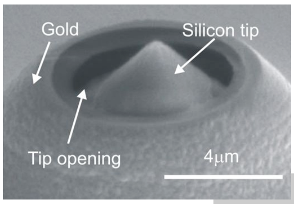
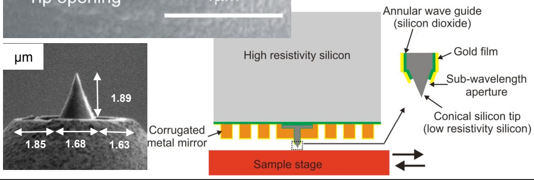


FIB-assisted THz tip fabrication and combination of THz nearfield microscopy with AFM



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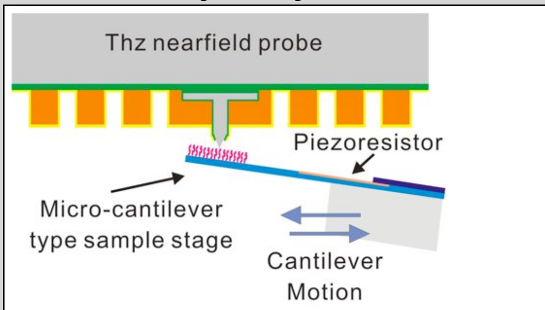

Combined THz-AFM – The trick with the sample …

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H. Shin, et al., manuscript in preparation (2008)   Mizaikoff, et al., patent granted (2008)

A View to a Kill(er Application …)

Analytical Chemistry vs. Physics perspective (mostly for condensed phase sensing …)

- **Ps are happy with few emission frequencies**
- **ACs want many different emission frequencies and a lot of power**

- **Ps want possibly narrow emission linewidths**
- **ACs basically don‘t care too much about the linewidth**

- **Ps are happy with a narrow tuning range**
- **ACs want the broadest tuning range possible**

- **Ps want to integrate lightsource and waveguide/cavity**
- **ACs want to separate lightsource and waveguide/cavity**

- **Ps believe the lightsource is the key component**
- **ACs believe the transducer is the key component**

Consequence – we need to collaborate!

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Acknowledgements

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