A Critical Analysis of THz Applications: The Intersection of Science and Technology

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We will consider the matching of technical approaches to applications in the THz spectral region. Particular attention will be paid to the physics of the interaction of the radiation and matter, how this physics leads to selection of technology, and, indeed, if the application is feasible. In many cases quantitative or semi-quantitative analyses are possible. Emphasis will be placed on using these analyses to identify especially attractive paths to applications that can be competitive for wide spread adoption. Specific results will be presented for both point and remote chemical sensors that are based on high resolution and brightness electronic sources. Sensitivity, specificity, and background clutter and interference will be considered quantitatively. Paths to low cost and compact THz electronic sensors will be described. Technical descriptions of the hardware implementations, analysis of the interactions of this hardware with the molecular signatures, and analysis methods will be presented.

DTRA
May 29, 2012
Ft. Belvior, VA

Content

Physics: A Guide to Applications and Appropriate Technology

Examples

- Point gas sensors
- Remote gas sensors
- Imaging
  - special alignment and illumination requirements
  - coherent effects (speckle)
- A few comments on bio

Implementation and Comparisons

- R & D base for the THz vs IR, MS/GC, etc.
- 6.1 Research

Paths Forward

- Near term based of well defined strengths (specificity, small sample, . .)
- What is possible with mature THz science and technology (broadening applicability)

The THz: A Useful Combination

Applications often based on combination of attributes:

Penetration
Angular Resolution
Spectroscopic Capability

At what frequency within the THz (0.1 – 10 THz) do we execute this compromise?

Attributes typically are steep powers of frequency

How do we choose an appropriate technology?

Figures of merit – especially power/dynamic range vs. brightness; orders of magnitude

Analysis needed to supplement qualitative concepts to choose useful paths forward.

“Whispered Excitement about the THz”

Graham Jordan

Opening Plenary Presentation
SPIE Symposium: Optics/Photonics in Security and Defense
Bruges, Belgium, 26 September, 2005

Goal today:

To sort through some of the hype and clutter so that we can better see the path forward in the THz (SMM, MM, FIR, NMM, . . .)

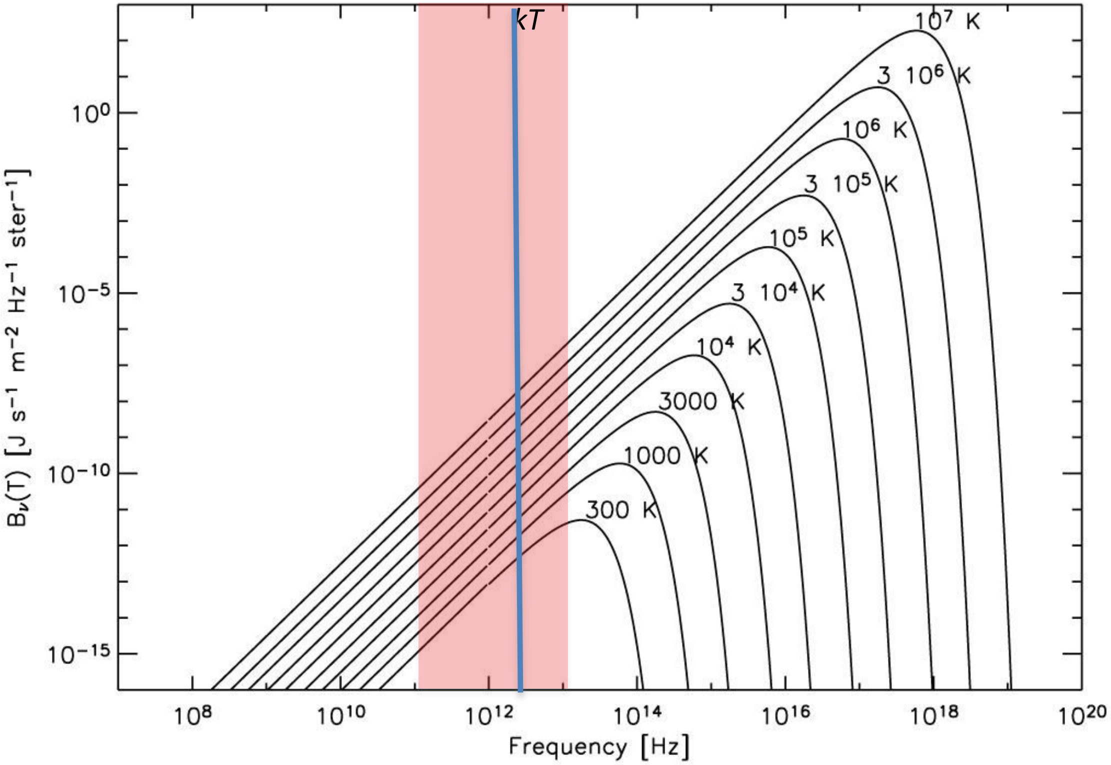
Themes:

There is a diversity of applications with similar technical requirements
Electronic technical approaches are very competitive
Leveraging the mass market is fundamental to success

The Physics:

A Guide to Applications and Appropriate Technology

Radiation and Interactions: Orders of Magnitude

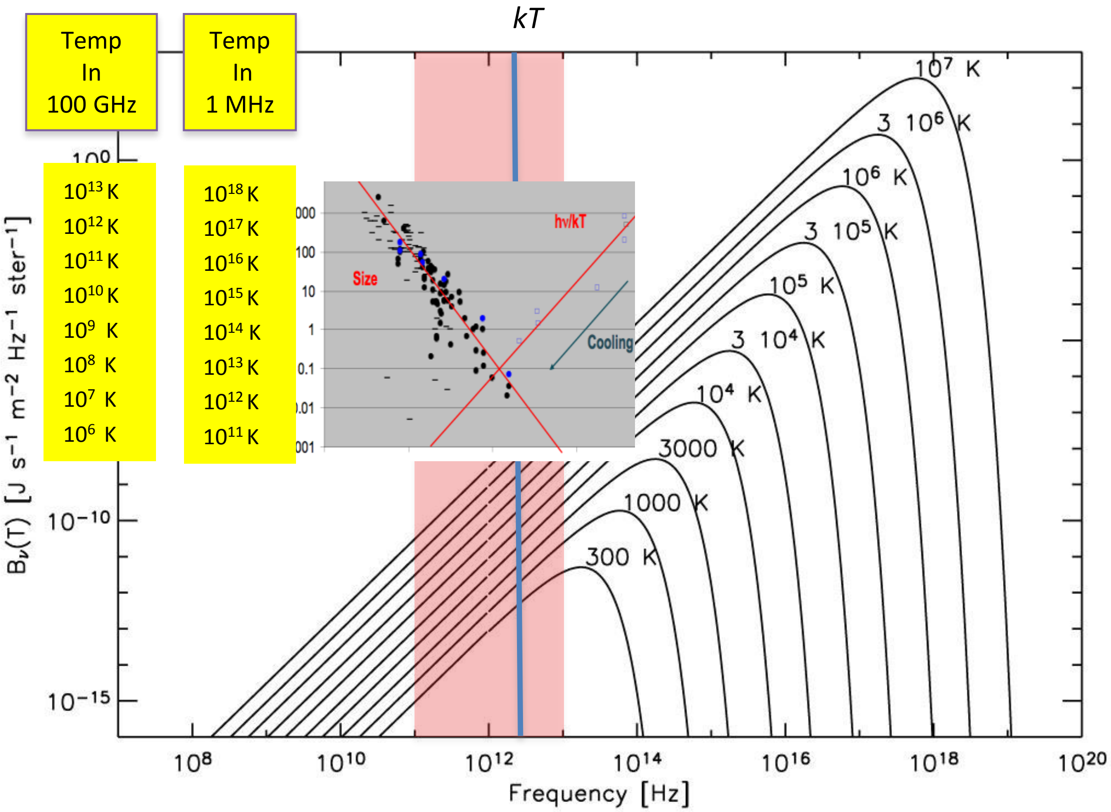


The THz has defined itself broadly and spans *kT*

Linewidths: Fundamental to both specificity and sensitivity

Doppler broadening is proportional to frequency: 0.1 – 10 MHz in THz : x 100 – x 1000 in IR
Atmospheric pressure broadening: 10 GHz at all frequencies
Sensors often purposefully pressure broadened to compensate for low spectrometer resolution
Solids: 100's GHz – to continua (typically at high THz to IR frequencies),
but crystals and ordered solids can be much narrower, especially at very low temperatures

Radiation and Interactions: Orders of Magnitude



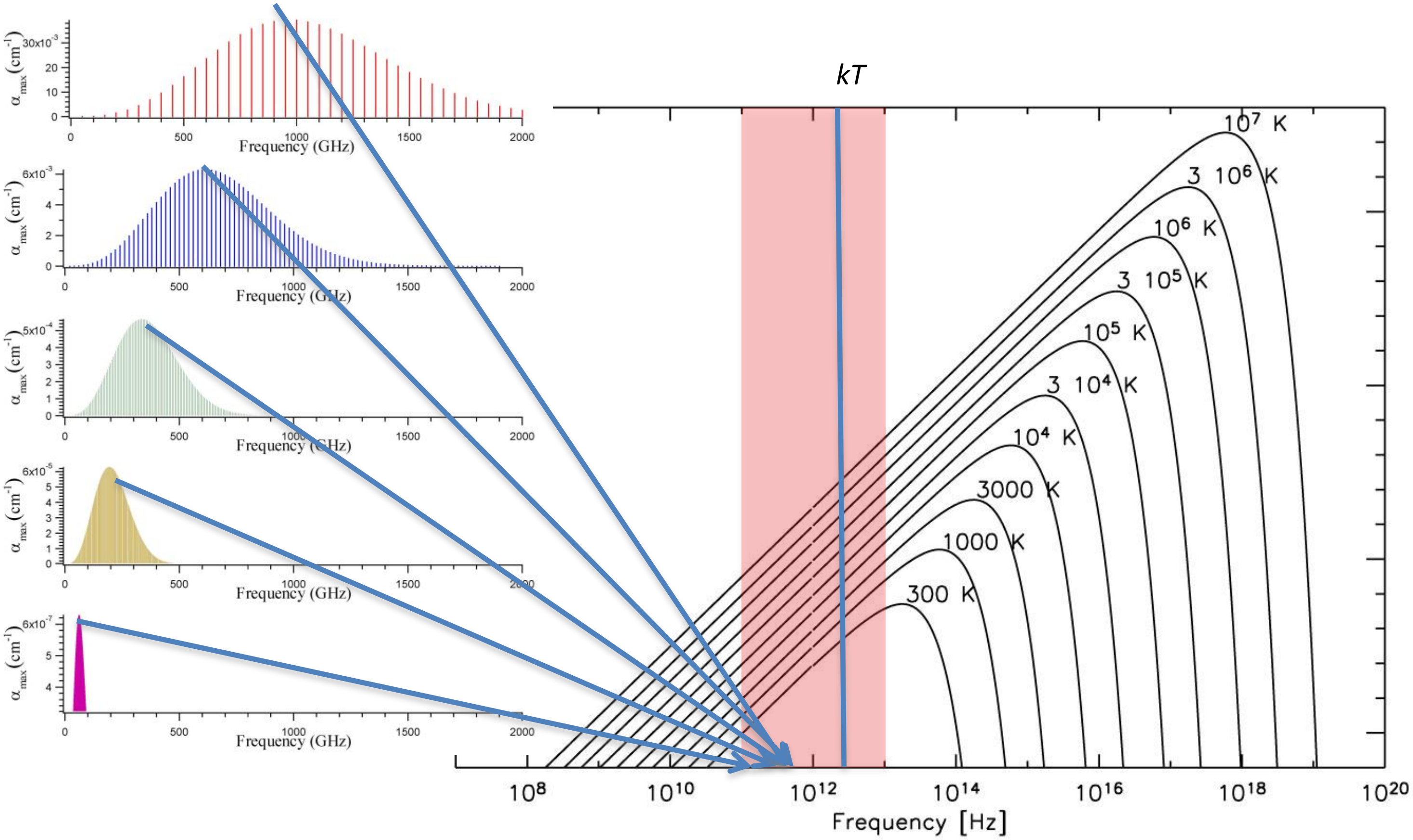
Temp In 100 GHz	Temp In 1 MHz
10^{13} K	10^{18} K
10^{12} K	10^{17} K
10^{11} K	10^{16} K
10^{10} K	10^{15} K
10^{9} K	10^{14} K
10^{8} K	10^{13} K
10^{7} K	10^{12} K
10^{6} K	10^{11} K

Jumping the ‘gap in the electromagnetic spectrum’ is not the same as closing it.

Bandwidth matters

- **1 mW in 1 MHz is equivalent to 10^{14} K**
- **Must use appropriate figures of merit: total power (W) (dynamic range?) vs. brightness (W/Hz)**

Radiation and Interactions: Orders of Magnitude

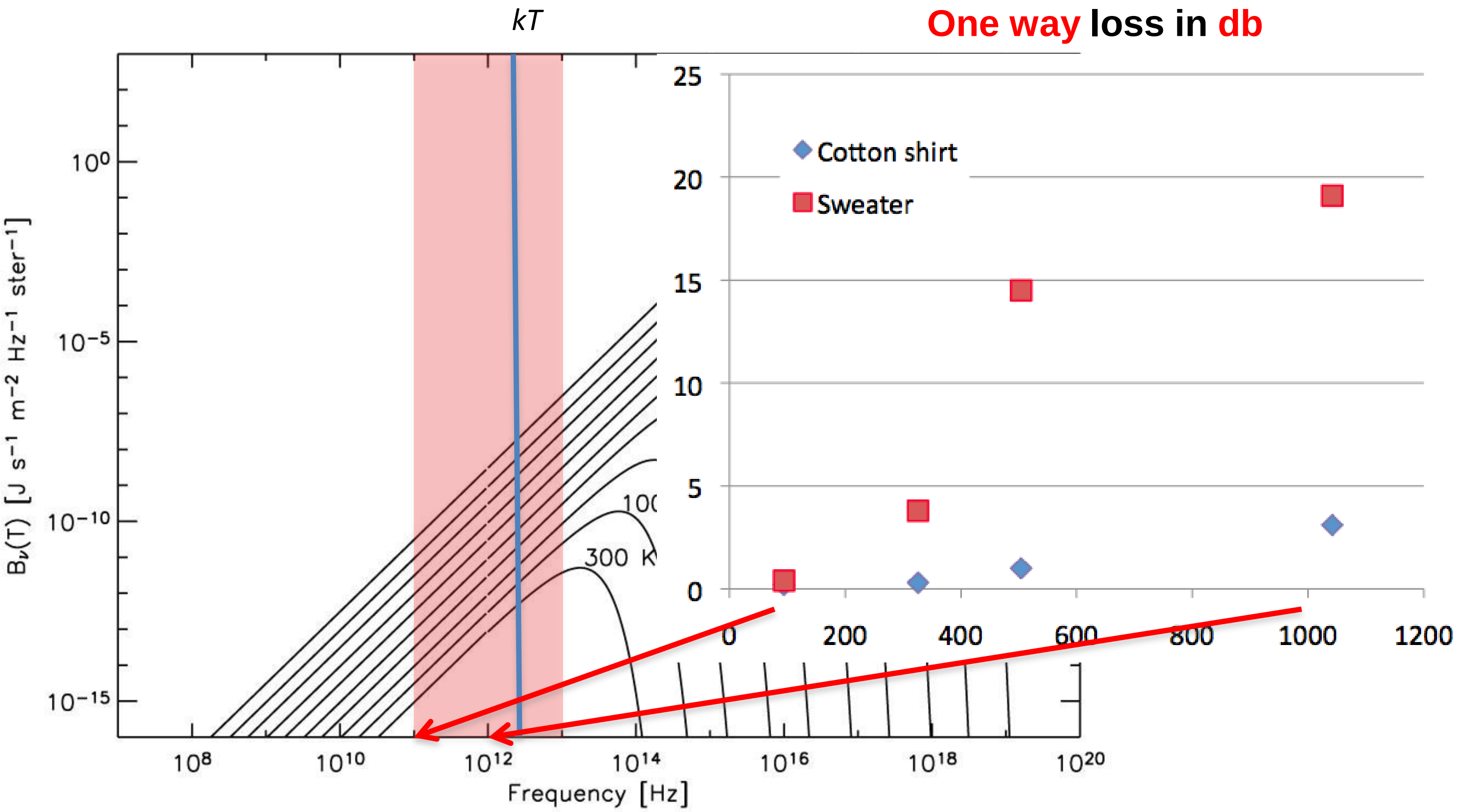


Peak interaction strength is molecule dependent

Sensors typically demonstrated on atypical, small, very favorable molecules (H_2O, NH_3, CO, . . .)

Maximum strength occurs more typically at order of 300 GHz

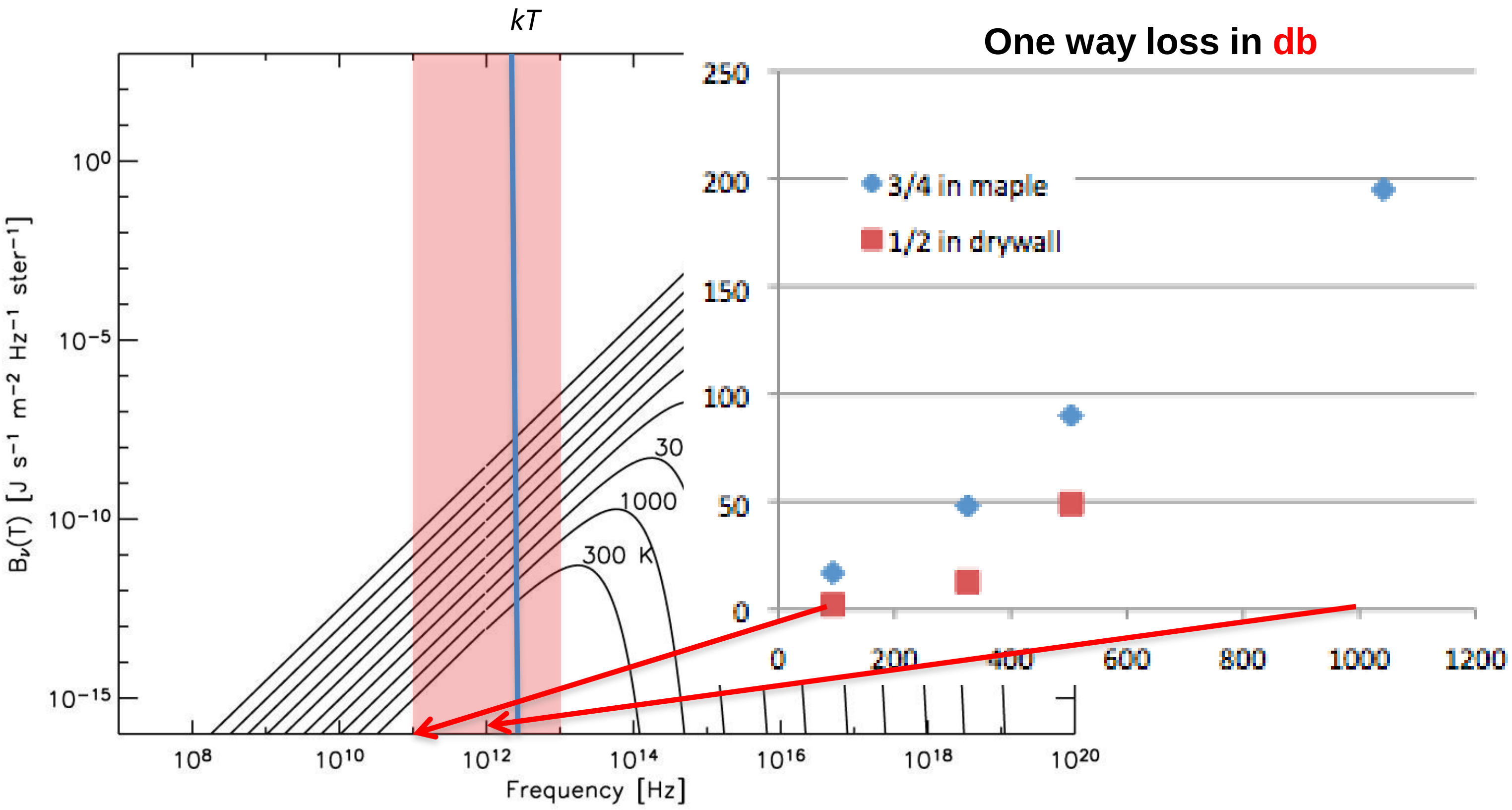
Radiation and Interactions: Orders of Magnitude



Penetration is an extremely steep function of frequency

Can we see through clothes? Yes – in the low THz

Radiation and Interactions: Orders of Magnitude



Penetration is an extremely steep function of frequency

Can we see through walls? No – unless we live in straw or foam houses

System Design - I

IEEE TRANSACTIONS ON TERAHERTZ SCIENCE AND TECHNOLOGY, VOL. 1, NO. 1, SEPTEMBER 2011

Explosives Detection by Terahertz Spectroscopy—A Bridge Too Far?

Michael C. Kemp, *Member, IEEE*

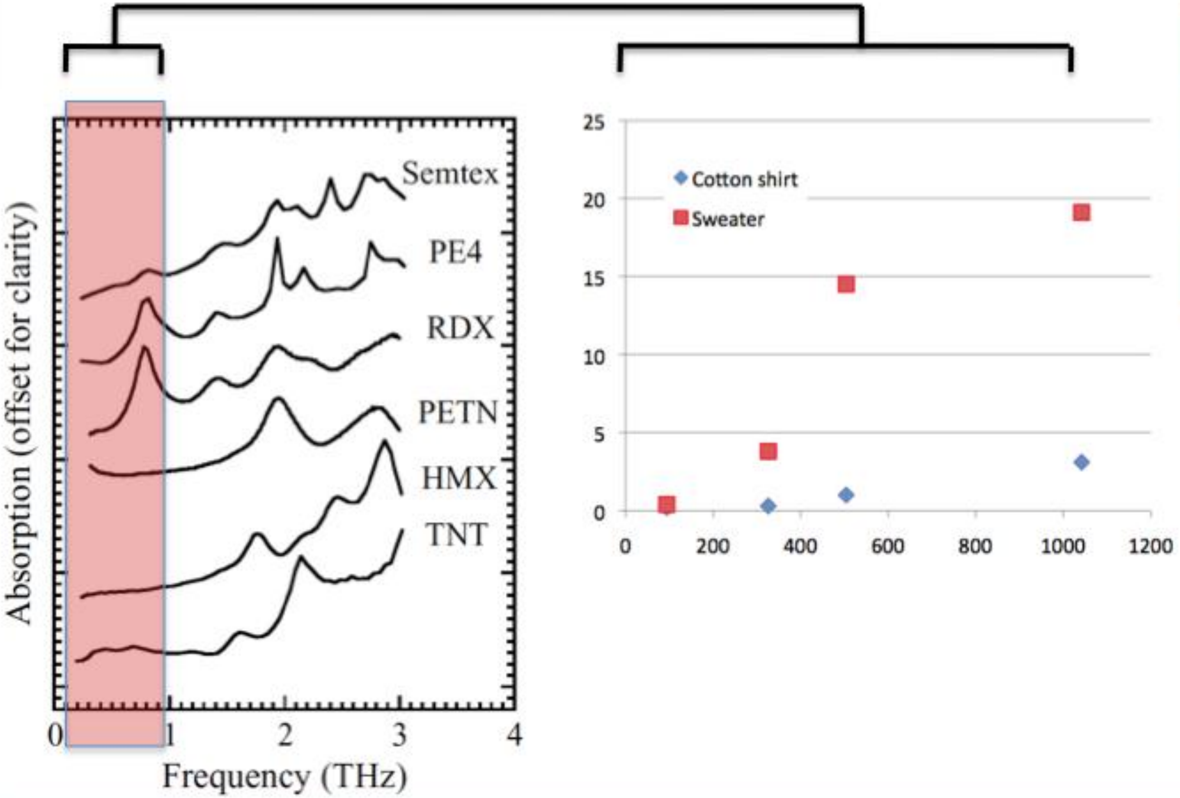
Considerations

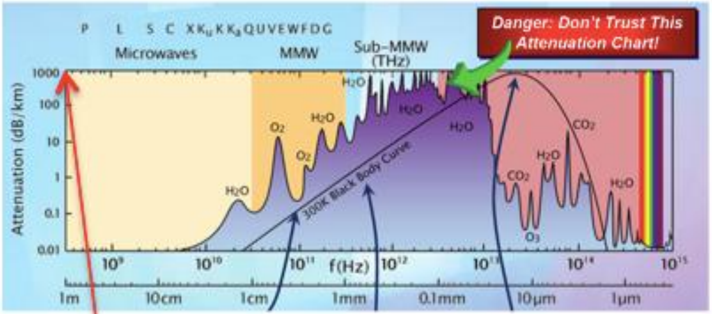
Transmission at frequencies of spectra?

Uniqueness of observable spectra?

Reflection spectra vs transmission?

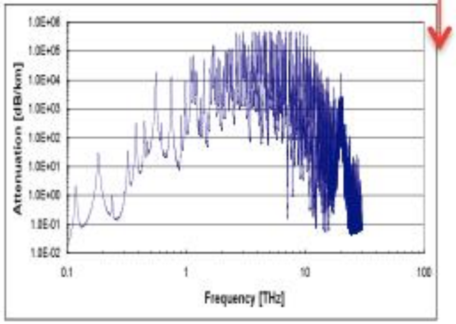
Atmospheric transmission
(even at 0.1 – 1 m standoff)?





Danger: Don't Trust This Attenuation Chart!

1000 db/km vs 100 000 db/km



A Few Comments on Bio

I am not an expert and it deserves a fair hearing from those that are

There is clear a lot of nonsense, but that doesn’t mean that everything is nonsense

Sometimes even something that is wrong, leads to good things

Gravity wave detection – Spectroscopy of skin cancer

1. **Bio is very important**

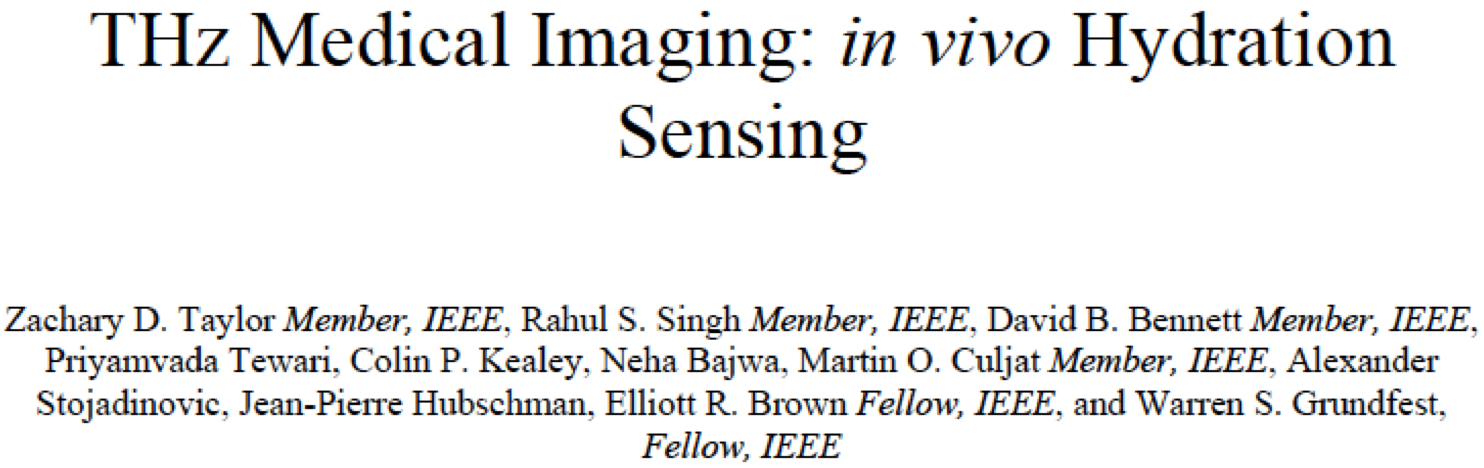
2. **There have been many reports of THz bio sensors**

3. **To the best of my knowledge, no two laboratories have reported confirming THz results (except for the fact that water has a different contrast in bio systems), except perhaps at frequencies that are really IR.**

4. **If I were an ambitious PM, I would host a bio workshop with the theme of reproducible THz bio spectra. You may recall that a number of years ago a number of well know THz laboratories published THz spectra of explosives that were all different. It wasn't until Mike Kemp published his results that everyone converged on the right answer and even got the same results using THz-TDS and traditional FTFIR spectroscopy.**

5. **To put a positive twist on this, one might invite contributions on sample preparation and its impact on observed signatures.**

System Design - II



THz Medical Imaging: *in vivo* Hydration Sensing

Zachary D. Taylor *Member, IEEE*, Rahul S. Singh *Member, IEEE*, David B. Bennett *Member, IEEE*, Priyamvada Tewari, Colin P. Kealey, Neha Bajwa, Martin O. Culjat *Member, IEEE*, Alexander Stojadinovic, Jean-Pierre Hubschman, Elliott R. Brown *Fellow, IEEE*, and Warren S. Grundfest, *Fellow, IEEE*

IEEE Transactions on Terahertz Science and Technology
Special Inaugural Issue: Vol. 1, No. 1, Sept. 2011, pp. 201-219.

Examples

(How the physics drives system choices)

Point Gas Sensors

Remote Gas Sensors

THz Imaging

Background and Status

Basic Submillimeter Spectroscopy Established: ARO, NSF, NASA, etc
Basic Spectroscopy, Chemical Physics, Quantum Electronics, Astrophysics, Atmospheric Science

Sensor Parameters and Character laid out: *Analytical Chemistry* Nov 1998

Solid State Implementation: DARPA/MTO THz program (2000 – 2004)

Proof of Principle Seedlings (DARPA/STO) (2003 – 2006)

Mission Adaptable Chemical Sensor (MACS) (2006 – 2008)
(With Battelle, Smart Transitions, and Enthalpy)

Breath Analysis (DARPA) (2009 –2010)
(With Battelle)

Large Molecule Limit Study (ARO) (2009 –

CMOS and miniaturization (SRC, Texas Instruments, IBM) (2009 –

The Current System (Phase I MACS)

Designed to meet DARPA's redone Phase I go/nogo in 12/18 months

Number of gases reduced to >30 **(PFA < 10^{-4} required, << 10^{-10} demonstrated)**

Only demonstrate 1 gas with sorbent system **(< 100 ppt required, <2 ppt demonstrated)**

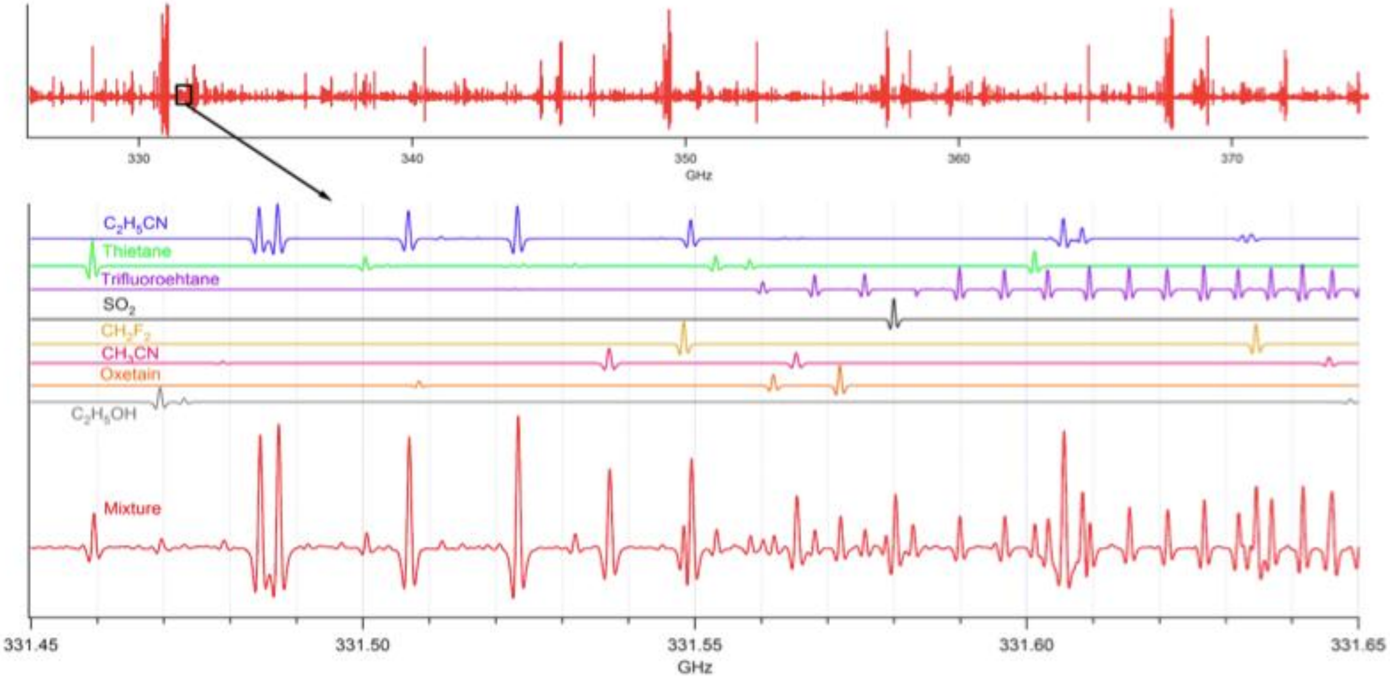
R & D deferred (larger molecules/higher pressures)

1 cu ft packaging moved from Phase II to Phase I

=> Much of the research to generalize and demonstrate the technique was not done

Initial DARPA Clutter/Uniqueness Challenge:

Correctly identify components of mixture of 20 gases blindly selected from set of 30



Clutter sensitivity limit ~ 1 ppt in polluted atmosphere

Line width < 1 MHz (>10^5) resolution elements

CO_2 has no spectra, H_2O sparse (~1 line/10^5 resolution elements)

Electronic sources allow line subtraction at < 0.01 MHz resolution

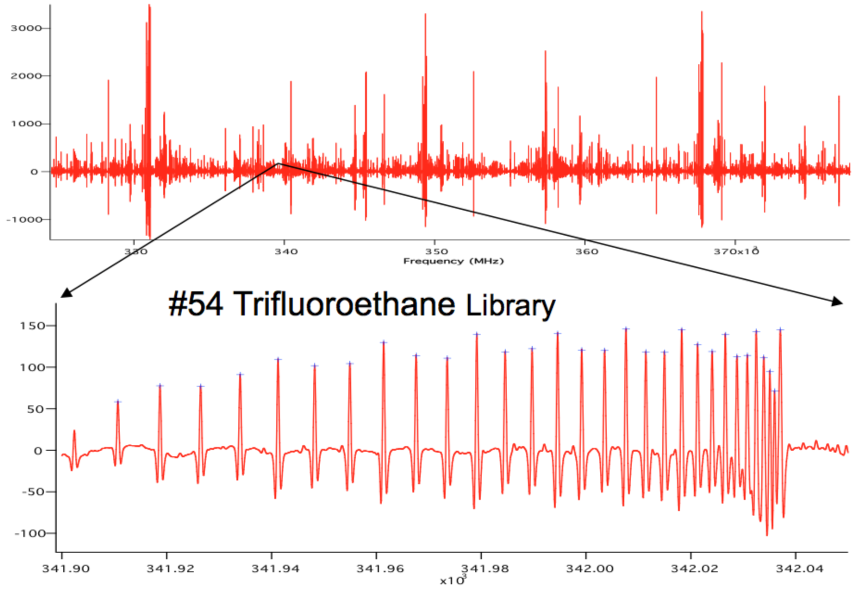
Impact of atmospheric clutter on Doppler-limited gas sensors in the submillimeter/terahertz

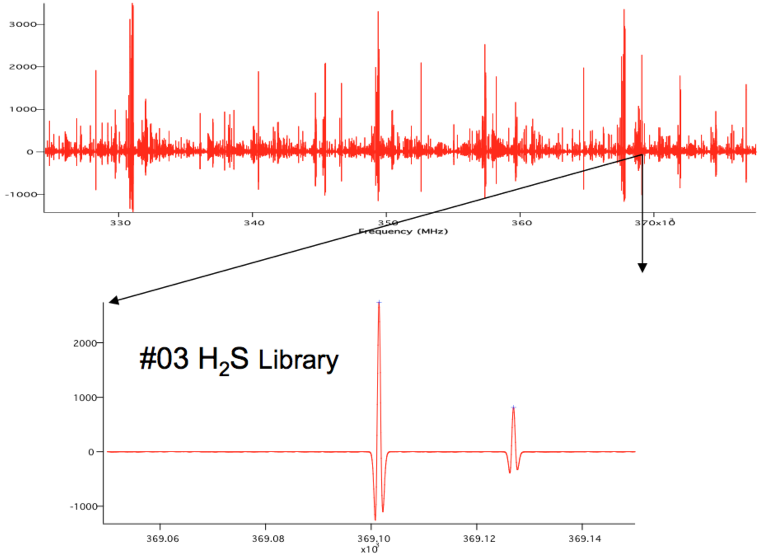
Ivan R. Medvedev,[1] Christopher F. Neese,[2] Grant M. Plummer,[3] and Frank C. De Lucia[2,*]

APPLIED OPTICS / Vol. 50, No. 18 / 20 June 2011

Spectral Density

Impact of Molecular Size/Weight


#54 Trifluoroethane Library


#03 H_2S Library

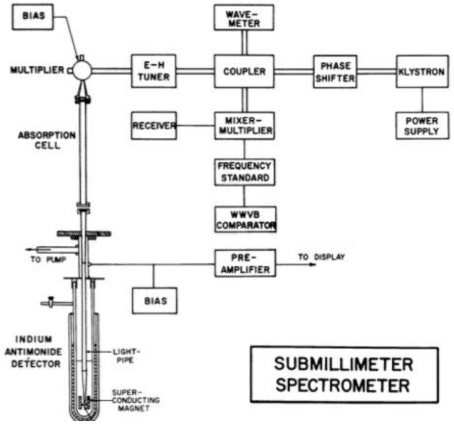
The rapid rise of spectral density with molecular size is fundamental and underlies the limits to generality for spectroscopic sensors

Frequency Multiplication Technology

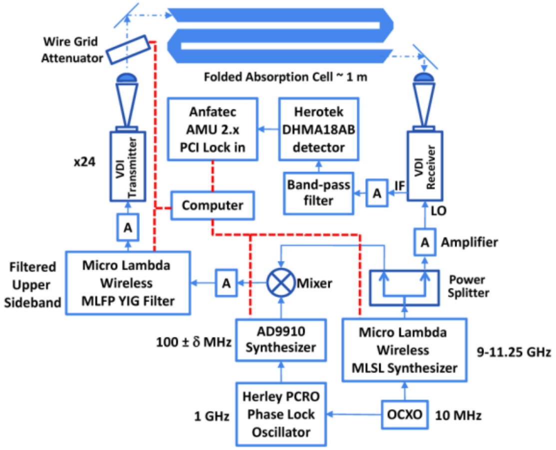
[The technology choice matters]

High Spectral purity
Frequency calibration and agility
High spectral brightness [W/Hz]

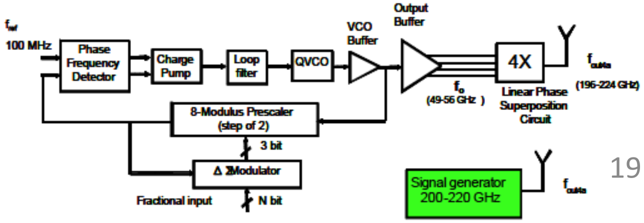
1970: Tubes and cryogenics



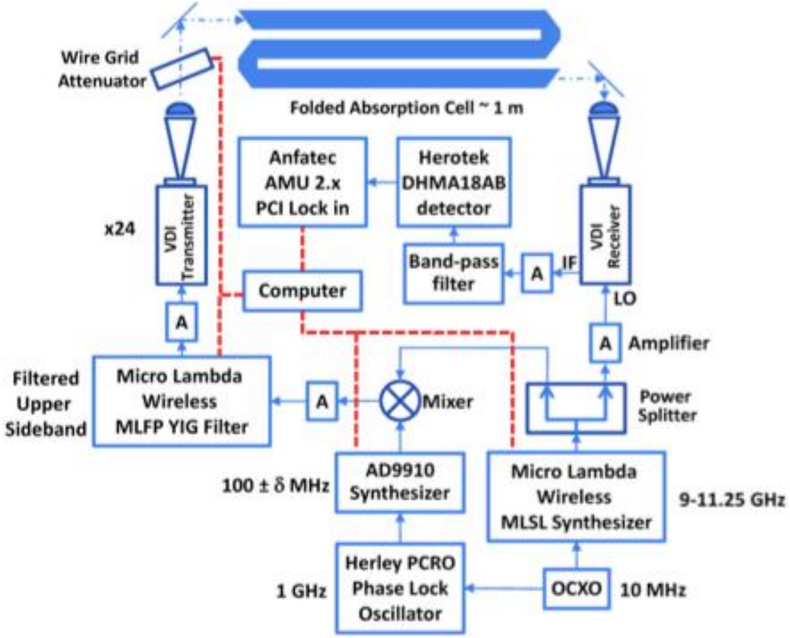
Now: Solid state waveguide block and COT integration



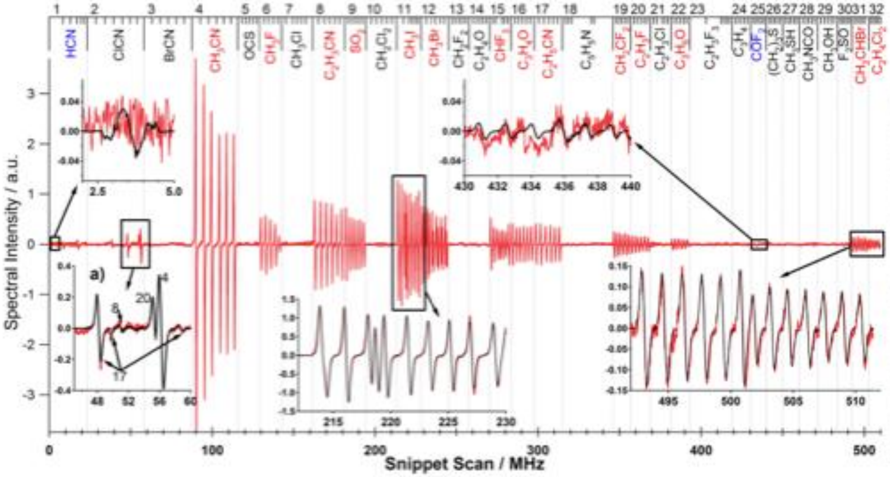
Future: Chip level integration



A Packaged Sensor Overview



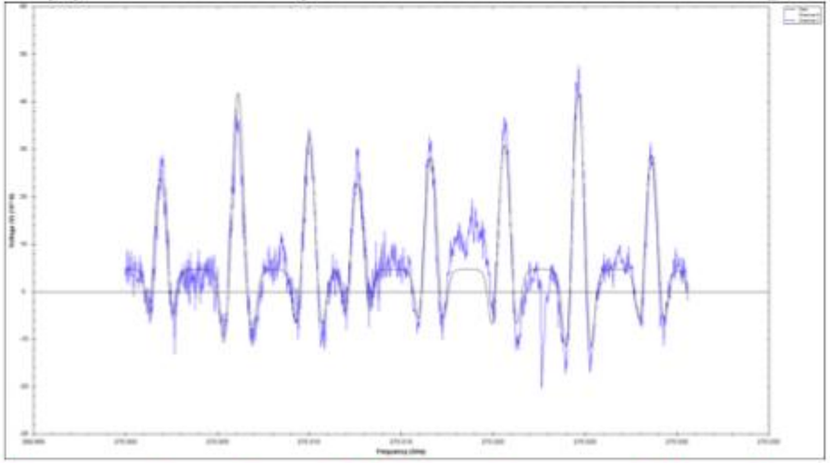
Absolute' specificity on mixture of 32 gases



	Pressure /µtorr	S/N
1	0.06	5.0
2	0.00	0.4
3	0.02	1.3
4	61.79	598.2
5	-0.02	0.5
6	26.97	304.7
7	0.00	0.1
8	66.09	432.5
9	54.13	323.8
10	0.12	1.2
11	130.10	404.2
12	85.04	390.4
13	0.16	1.0
14	-0.02	0.1
15	70.05	273.0
16	58.93	281.2
17	60.61	321.7
18	-0.12	0.8
19	55.67	192.8
20	40.31	161.3
21	-0.55	2.0
22	30.09	92.8
23	-0.07	0.3
24	-0.16	0.5
25	4.68	9.5
26	-0.90	1.8
27	0.10	0.2
28	0.81	1.5
29	0.27	0.6
30	-0.63	1.1
31	71.78	123.2
32	73.12	82.6

Σ = 0.89 mtorr

2 ppt sensitivity demonstrated on one gas



Enabled by:

(1) High brightness temperature of electronic sources (~10^{14} K)

(2) Frequency accuracy and agility of electronic synthesized sources

Townes noise is a many orders of magnitude effect in spectrometers that is not present in radar, etc.

System Numbers

For a receiver noise temperature $T_N = 3000$ K and $b = B = 10^6$ Hz, $P_N = 5 \times 10^{-14}$ W. $P_c = 10^{-3}$ W

$$\frac{P_c}{P_N} \sim 10^{10}$$

If we have a carrier power of $P_c = 1$ mW, we must also consider the noise associated with the adding of the blackbody noise *voltage* with the carrier.

For this case

$$P_n' \approx \sqrt{kT\Delta \nu P_c} = \sqrt{(5 \times 10^{-14})(10^{-3})} \approx 10^{-8}\,W$$

Five Orders of Magnitude

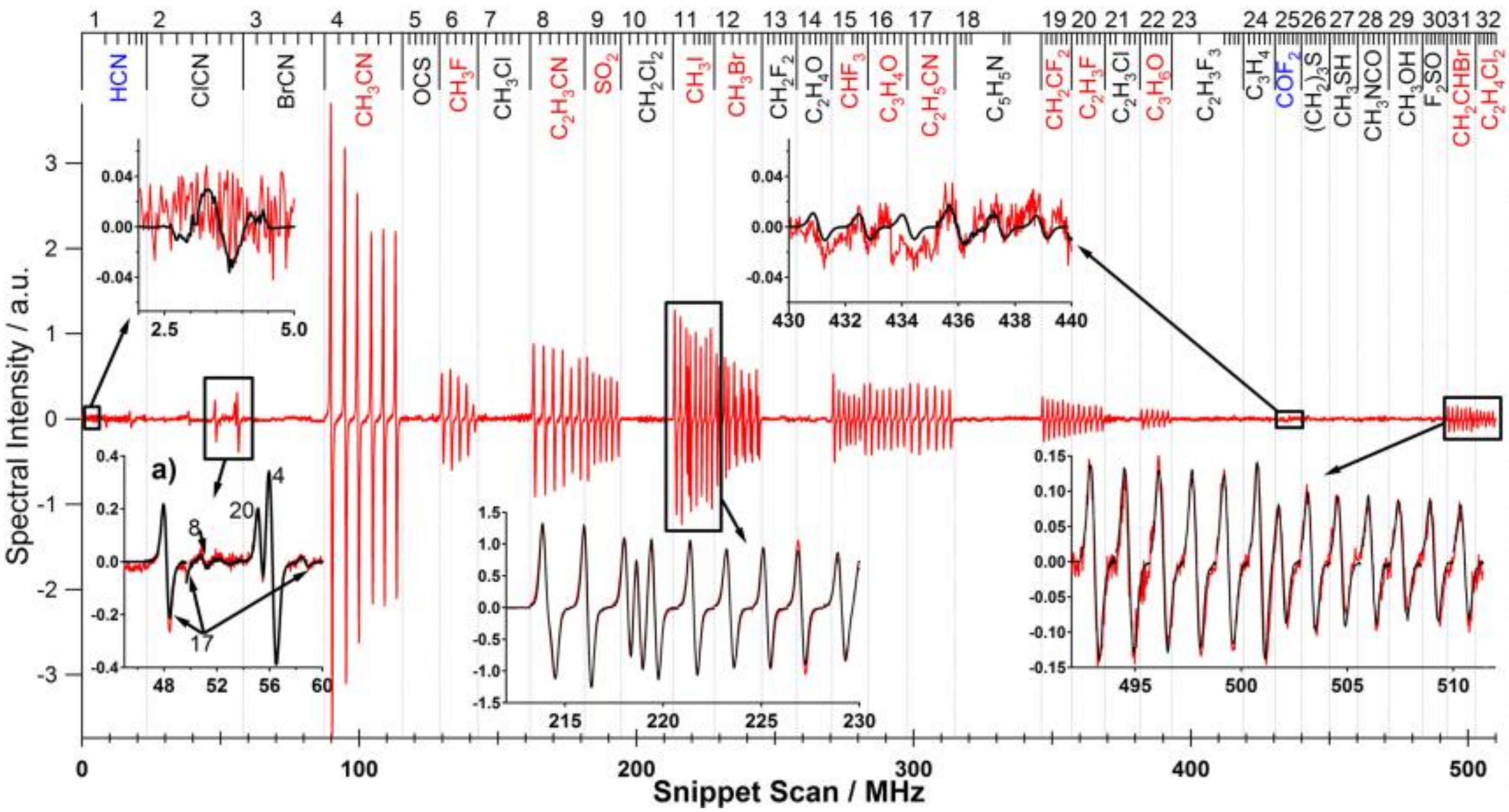
This is about five orders of magnitude above the receiver noise.

For 1 μsec integration the system S/N is then

$$S/N = \frac{P_c}{P_N'} \sim \frac{10^{-3}\,W}{10^{-8}\,W} \sim 10^5$$

This is the impact of the so called ‘Townes Noise’.

Impact is only large when we are looking to detect a small change in a large P_c



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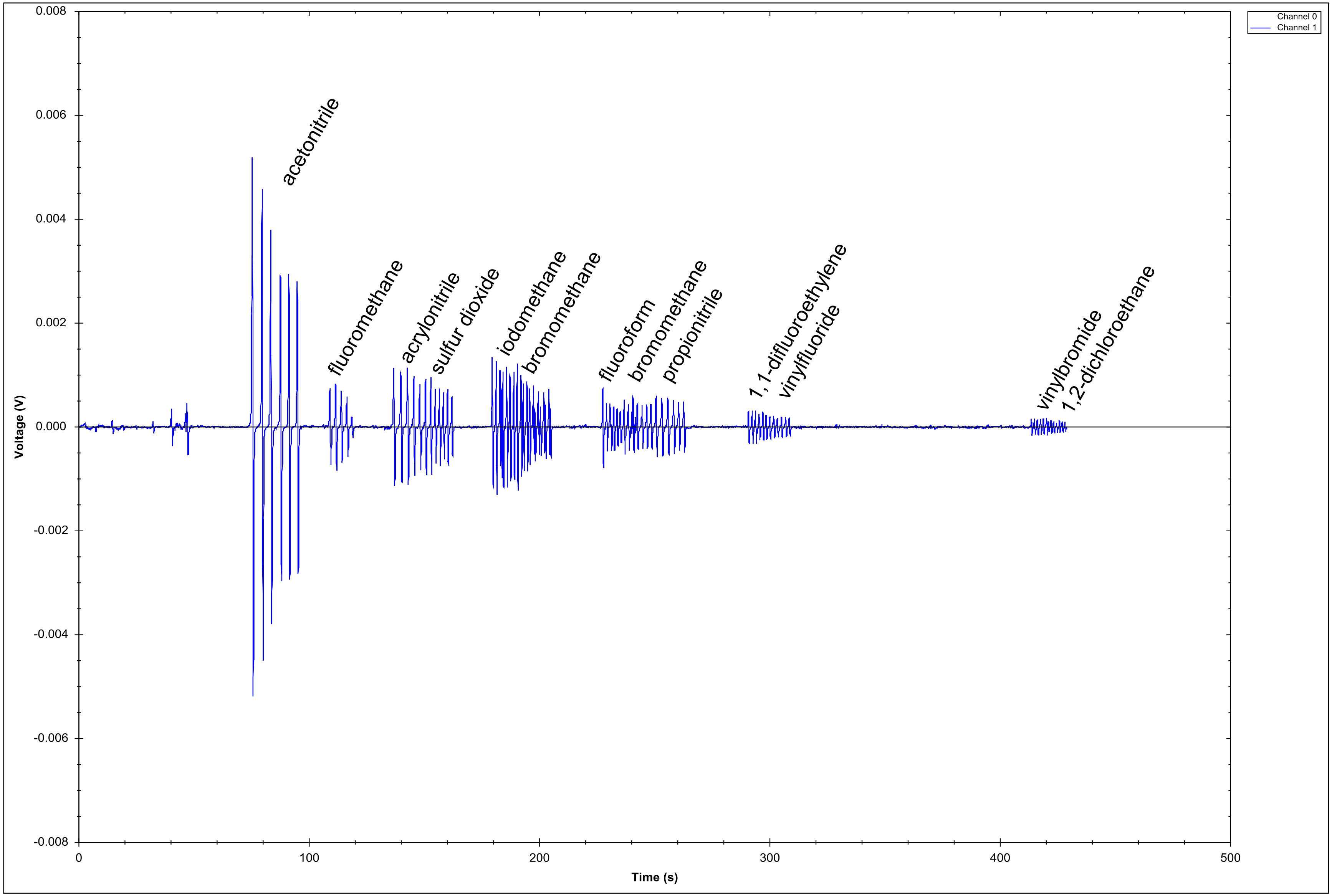
∑ = 0.89 mtorr

System scans six (selectable) snippets for each of 32 (selectable) chemicals
Compares the resultant spectra with an intensity calibrated library
Does LSQ to determine concentrations

Additional material: **Testing procedure and additional detail are given in the report of the MACS Evaluation Team (MET) and the OSU report to that team.**


Channel 0
Channel 1
Voltage (V)
0.008
0.006
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
Time (s)
0
100
200
300
400
500
acetonitrile
fluoromethane
acrylonitrile
sulfur dioxide
iodomethane
bromomethane
fluoroform
bromomethane
propionitrile
1,1-difluoroethylene
vinylfluoride
vinylbromide
1,2-dichloroethane

System Design Space

How much space do you have? White Cells or equivalent?

How much power do you have? Saturation limit

How do you avoid spending photons on white space?

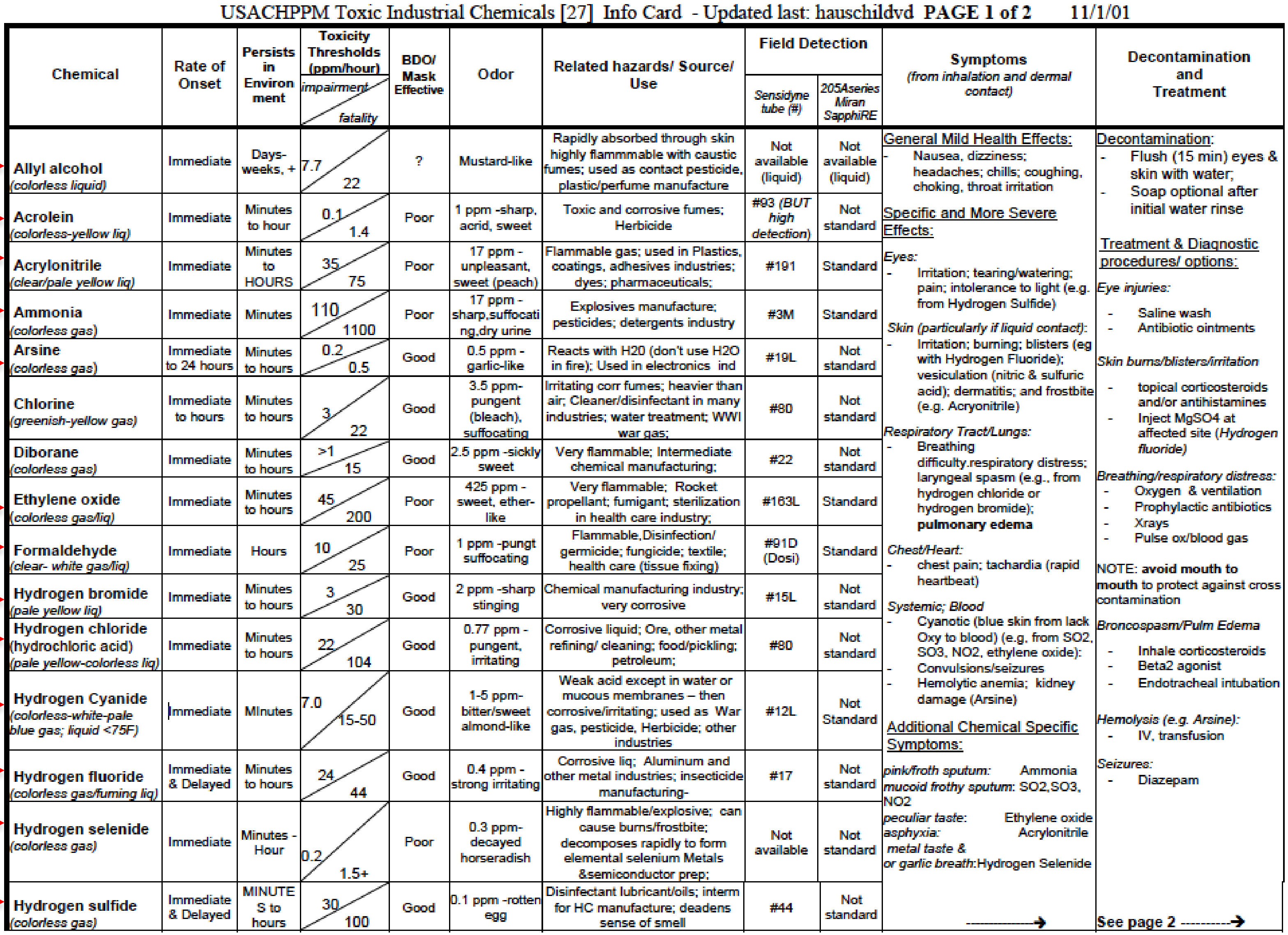
many molecules/crowded spectra vs sparse spectra

How adaptable is the system architectures to varying requirements?

How scalable is the approach?

Market technology?

Broad Coverage of TIC Gases

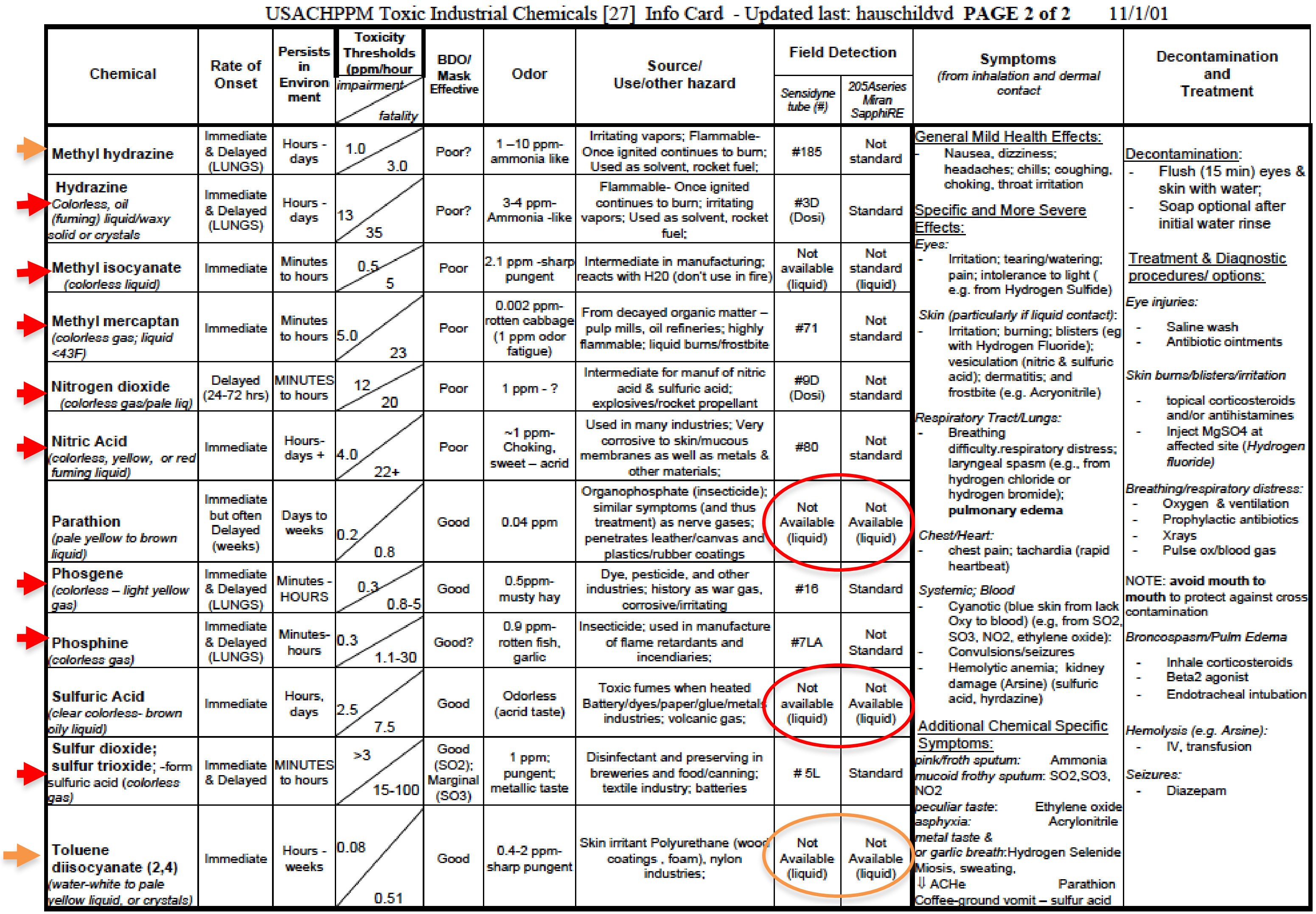


USACHPPM Toxic Industrial Chemicals [27] Info Card - Updated last: hauschildvd PAGE 1 of 2 11/1/01

Chemical	Rate of Onset	Persists in Environment	Toxicity Thresholds (ppm/hour)		BDO/ Mask Effective	Odor	Related hazards/ Source/ Use	Field Detection		Symptoms *(from inhalation and dermal contact)*	Decontamination and Treatment
			impairment	*fatality*				*Sensidyne tube (#)*	*205Aseries Miran SapphiRE*		
Allyl alcohol *(colorless liquid)*	Immediate	Days-weeks, +	7.7	22	?	Mustard-like	Rapidly absorbed through skin highly flammmable with caustic fumes; used as contact pesticide, plastic/perfume manufacture	Not available (liquid)	Not available (liquid)	General Mild Health Effects: - Nausea, dizziness; headaches; chills; coughing, choking, throat irritation Specific and More Severe Effects: *Eyes:* - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide) *Skin (particularly if liquid contact):* - Irritation; burning; blisters (eg with Hydrogen Fluoride); vesiculation (nitric & sulfuric acid); dermatitis; and frostbite (e.g. Acryonitrile) *Respiratory Tract/Lungs:* - Breathing difficulty.respiratory distress; laryngeal spasm (e.g., from hydrogen chloride or hydrogen bromide); **pulmonary edema** *Chest/Heart:* - chest pain; tachardia (rapid heartbeat) *Systemic; Blood* - Cyanotic (blue skin from lack Oxy to blood) (e.g. from SO2, SO3, NO2, ethylene oxide): - Convulsions/seizures - Hemolytic anemia; kidney damage (Arsine) Additional Chemical Specific Symptoms: *pink/froth sputum:* Ammonia *mucoid frothy sputum:* SO2,SO3, NO2 *peculiar taste:* Ethylene oxide *asphyxia:* Acrylonitrile *metal taste & or garlic breath:* Hydrogen Selenide ------------→	Decontamination: - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse Treatment & Diagnostic procedures/ options: *Eye injuries:* - Saline wash - Antibiotic ointments *Skin burns/blisters/irritation* - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (*Hydrogen fluoride)* *Breathing/respiratory distress:* - Oxygen & ventilation - Prophylactic antibiotics - Xrays - Pulse ox/blood gas NOTE: **avoid mouth to mouth** to protect against cross contamination *Broncospasm/Pulm Edema* - Inhale corticosteroids - Beta2 agonist - Endotracheal intubation *Hemolysis (e.g. Arsine):* - IV, transfusion *Seizures:* - Diazepam **See page 2** ---------→
Acrolein *(colorless-yellow liq)*	Immediate	Minutes to hour	0.1	1.4	Poor	1 ppm -sharp, acrid, sweet	Toxic and corrosive fumes; Herbicide	#93 *(BUT high detection)*	Not standard		
Acrylonitrile *(clear/pale yellow liq)*	Immediate	Minutes to HOURS	35	75	Poor	17 ppm - unpleasant, sweet (peach)	Flammable gas; used in Plastics, coatings, adhesives industries; dyes; pharmaceuticals;	#191	Standard		
Ammonia *(colorless gas)*	Immediate	Minutes	110	1100	Poor	17 ppm - sharp,suffocating,dry urine	Explosives manufacture; pesticides; detergents industry	#3M	Standard		
Arsine *(colorless gas)*	Immediate to 24 hours	Minutes to hours	0.2	0.5	Good	0.5 ppm - garlic-like	Reacts with H2O (don't use H2O in fire); Used in electronics ind	#19L	Not standard		
Chlorine *(greenish-yellow gas)*	Immediate to hours	Minutes to hours	3	22	Good	3.5 ppm- pungent (bleach), suffocating	Irritating corr fumes; heavier than air; Cleaner/disinfectant in many industries; water treatment; WWI war gas;	#80	Not standard		
Diborane *(colorless gas)*	Immediate	Minutes to hours	>1	15	Good	2.5 ppm -sickly sweet	Very flammable; Intermediate chemical manufacturing;	#22	Not standard		
Ethylene oxide *(colorless gas/liq)*	Immediate	Minutes to hours	45	200	Poor	425 ppm - sweet, ether-like	Very flammable; Rocket propellant; fumigant; sterilization in health care industry;	#163L	Standard		
Formaldehyde *(clear- white gas/liq)*	Immediate	Hours	10	25	Poor	1 ppm -pungt suffocating	Flammable,Disinfection/ germicide; fungicide; textile; health care (tissue fixing)	#91D (Dosi)	Standard		
Hydrogen bromide *(pale yellow liq)*	Immediate	Minutes to hours	3	30	Good	2 ppm -sharp stinging	Chemical manufacturing industry; very corrosive	#15L	Not standard		
Hydrogen chloride (hydrochloric acid) *(pale yellow-colorless liq)*	Immediate	Minutes to hours	22	104	Good	0.77 ppm - pungent, irritating	Corrosive liquid; Ore, other metal refining/ cleaning; food/pickling; petroleum;	#80	Not standard		
Hydrogen Cyanide *(colorless-white-pale blue gas; liquid <75F)*	Immediate	MInutes	7.0	15-50	Good	1-5 ppm- bitter/sweet almond-like	Weak acid except in water or mucous membranes – then corrosive/irritating; used as War gas, pesticide, Herbicide; other industries	#12L	Not Standard		
Hydrogen fluoride *(colorless gas/fuming liq)*	Immediate & Delayed	Minutes to hours	24	44	Good	0.4 ppm - strong irritating	Corrosive liq; Aluminum and other metal industries; insecticide manufacturing-	#17	Not standard		
Hydrogen selenide *(colorless gas)*	Immediate	Minutes - Hour	0.2	1.5+	Poor	0.3 ppm- decayed horseradish	Highly flammable/explosive; can cause burns/frostbite; decomposes rapidly to form elemental selenium Metals &semiconductor prep;	Not available	Not standard		
Hydrogen sulfide *(colorless gas)*	Immediate & Delayed	MINUTES to hours	30	100	Good	0.1 ppm -rotten egg	Disinfectant lubricant/oils; interm for HC manufacture; deadens sense of smell	#44	Not standard		

HCl

Simultaneous Recovery with 'Absolute Specificity' in Mixture



USACHPPM Toxic Industrial Chemicals [27] Info Card - Updated last: hauschildvd **PAGE 2 of 2** 11/1/01

Chemical	Rate of Onset	Persists in Environment	Toxicity Thresholds (ppm/hour		BDO/ Mask Effective	Odor	Source/ Use/other hazard	Field Detection		Symptoms *(from inhalation and dermal contact*	Decontamination and Treatment
			impairment	*fatality*				*Sensidyne tube (#)*	*205Aseries Miran SapphiRE*		
Methyl hydrazine	Immediate & Delayed (LUNGS)	Hours - days	1.0	3.0	Poor?	1 –10 ppm- ammonia like	Irritating vapors; Flammable- Once ignited continues to burn; Used as solvent, rocket fuel;	#185	Not standard	General Mild Health Effects: - Nausea, dizziness; headaches; chills; coughing, choking, throat irritation Specific and More Severe Effects: *Eyes:* - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide) *Skin (particularly if liquid contact):* - Irritation; burning; blisters (eg with Hydrogen Fluoride); vesiculation (nitric & sulfuric acid); dermatitis; and frostbite (e.g. Acryonitrile) *Respiratory Tract/Lungs:* - Breathing difficulty.respiratory distress; laryngeal spasm (e.g., from hydrogen chloride or hydrogen bromide); **pulmonary edema** *Chest/Heart:* - chest pain; tachardia (rapid heartbeat) *Systemic; Blood* - Cyanotic (blue skin from lack Oxy to blood) (e.g. from SO2, SO3, NO2, ethylene oxide): - Convulsions/seizures - Hemolytic anemia; kidney damage (Arsine) (sulfuric acid, hyrdazine) Additional Chemical Specific Symptoms: *pink/froth sputum:* Ammonia *mucoid frothy sputum:* SO2,SO3, NO2 *peculiar taste:* Ethylene oxide *asphyxia:* Acrylonitrile *metal taste &* *or garlic breath:* Hydrogen Selenide Miosis, sweating, ⇓ ACHe Parathion Coffee-ground vomit – sulfur acid	Decontamination: - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse Treatment & Diagnostic procedures/ options: *Eye injuries:* - Saline wash - Antibiotic ointments *Skin burns/blisters/irritation* - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (*Hydrogen fluoride)* *Breathing/respiratory distress:* - Oxygen & ventilation - Prophylactic antibiotics - Xrays - Pulse ox/blood gas NOTE: **avoid mouth to mouth** to protect against cross contamination *Broncospasm/Pulm Edema* - Inhale corticosteroids - Beta2 agonist - Endotracheal intubation *Hemolysis (e.g. Arsine):* - IV, transfusion *Seizures:* - Diazepam
Hydrazine *Colorless, oil (fuming) liquid/waxy solid or crystals*	Immediate & Delayed (LUNGS)	Hours - days	13	35	Poor?	3-4 ppm- Ammonia -like	Flammable- Once ignited continues to burn; irritating vapors; Used as solvent, rocket fuel;	#3D (Dosi)	Standard		
Methyl isocyanate *(colorless liquid)*	Immediate	Minutes to hours	0.5	5	Poor	2.1 ppm -sharp pungent	Intermediate in manufacturing; reacts with H20 (don't use in fire)	Not available (liquid)	Not standard (liquid)		
Methyl mercaptan *(colorless gas; liquid <43F)*	Immediate	Minutes to hours	5.0	23	Poor	0.002 ppm- rotten cabbage (1 ppm odor fatigue)	From decayed organic matter – pulp mills, oil refineries; highly flammable; liquid burns/frostbite	#71	Not standard		
Nitrogen dioxide *(colorless gas/pale liq)*	Delayed (24-72 hrs)	MINUTES to hours	12	20	Poor	1 ppm - ?	Intermediate for manuf of nitric acid & sulfuric acid; explosives/rocket propellant	#9D (Dosi)	Not standard		
Nitric Acid *(colorless, yellow, or red fuming liquid)*	Immediate	Hours- days +	4.0	22+	Poor	~1 ppm- Choking, sweet – acrid	Used in many industries; Very corrosive to skin/mucous membranes as well as metals & other materials;	#80	Not standard		
Parathion *(pale yellow to brown liquid)*	Immediate but often Delayed (weeks)	Days to weeks	0.2	0.8	Good	0.04 ppm	Organophosphate (insecticide); similar symptoms (and thus treatment) as nerve gases; penetrates leather/canvas and plastics/rubber coatings	Not Available (liquid)	Not Available (liquid)		
Phosgene *(colorless – light yellow gas)*	Immediate & Delayed (LUNGS)	Minutes - HOURS	0.3	0.8-5	Good	0.5ppm- musty hay	Dye, pesticide, and other industries; history as war gas, corrosive/irritating	#16	Standard		
Phosphine *(colorless gas)*	Immediate & Delayed (LUNGS)	Minutes- hours	0.3	1.1-30	Good?	0.9 ppm- rotten fish, garlic	Insecticide; used in manufacture of flame retardants and incendiaries;	#7LA	Not Standard		
Sulfuric Acid *(clear colorless- brown oily liquid)*	Immediate	Hours, days	2.5	7.5	Good	Odorless (acrid taste)	Toxic fumes when heated Battery/dyes/paper/glue/metals industries; volcanic gas;	Not available (liquid)	Not Available (liquid)		
Sulfur dioxide; sulfur trioxide; -form sulfuric acid *(colorless gas)*	Immediate & Delayed	MINUTES to hours	>3	15-100	Good (SO2); Marginal (SO3)	1 ppm; pungent; metallic taste	Disinfectant and preserving in breweries and food/canning; textile industry; batteries	# 5L	Standard		
Toluene diisocyanate (2,4) *(water-white to pale yellow liquid, or crystals)*	Immediate	Hours - weeks	0.08	0.51	Good	0.4-2 ppm- sharp pungent	Skin irritant Polyurethane (wood coatings , foam), nylon industries;	Not Available (liquid)	Not Available (liquid)		

MET Suggested 60 Gas List for Phase II

Hydrogen Cyanide
Cyanogen Chloride
Cyanogen Bromide
Methyl Cyanide
Carbonyl Sulfide
Methyl Fluoride
Methyl Chloride
Acrylonitrile
Sulfur dioxide
Dichloromethane
Methyl Iodide
Methyl Bromide
Difluoromethane
Ethylene oxide
Trifluoromethane
Acrolein
Propionitrile
Pyridine
1,1 Difluoroethylene
Vinyl Fluoride
Vinyl Chloride
Oxetane
1,1,1 Trifluroethane
Propyne
Carbonyl Fluoride
Thietane
Methanethiol
Methyl isocyanate
Methanol
Thionyl fluoride
vinyl bromide

1,2 dichloroethane
Hydrogen Chloride
Hydrogen Bromide
Carbon Monoxide
Nitric Oxide
Ammonia
Hydrogen Sulfide
Hydrogen Selenide
Nitrogen Dioxide
Arsine
Phosphorous Trichloride
Phosphine
Hypochlorous acid
Phosphorus Trichloride
Formaldehyde
Nitric Acid
Chloroform
Phosgene
Nitromethane
Methylamine
Dimethyl Sulfate
Dimethyl Ether
GA (Tabun)
GB (Sarin)
GD (Soman)
VX
HD (sulfur mustard)
L (Lewisite)
HN (nitrogen mustard)
GF (cyclosarin)

MACS Phase I molecules in black

Suggested Phase II additions in red

Stark and Cavities in Phase II to extend large molecule frontier

Requested Comparisons (w/o Sorbents)

	SMM 1.5 m Cell 10 mTorr [2]	THz-TDS 5 m White Cell 7.5 mTorr[2] [3]	DFG in GaSe 600 Torr[3] [4]	Optical Comb/Cavity 100 Torr[1] [5, 6]
Number of gases	32	1	1 - 2	2 - 4
$\Delta\nu_{system}$	0.5 MHz	3000 MHz	5000 MHz	1600 MHz
$\Delta\nu_{instrument}$	0.001 MHz	3000 MHz	5000 MHz	800 MHz
NH_3	52 ppb 2.7 x10^{-14} mole	---	---	18 ppb 9.6x10^{-11} mole
CO	280 ppb 1.5 x10^{-13} mole	---	---	900 ppb 4.8x10^{-9} mole
HCN	10 ppb 5.3 x10^{-15} mole	---	---	---
CH_3CN	50 ppb 2.7 x10^{-14} mole	---	---	---
CH_3Cl	---	$10^9/10^4$ ppb[5] 4 x $10^{-7}/10^{-12}$ mole	---	---
HBr	---	---	HBr 150 000 ppm ~10^{-4} mole	---

Optical Comb/Cavity:

- **Similar ppx sensitivity**
- **requires 10^4 more sample – sorbent difficult**
- **has >10^4 lower resolution**
- **orders of magnitude more atmospheric clutter**
- **much larger and more complex**

THz Photomixer:

- **has >10^4 less ppx sensitivity**
- **requires 10^8 more sample – sorbent difficult**
- **demonstrates > 1000 less resolution**
- **orders of magnitude more atmospheric clutter**
- **somewhat larger and more complex (8 cu ft)**

How can this be?

- **source brightness (W/Hz)**
- **Doppler and Pressure broadening resolution**
- **source agility and frequency calibration**
- **Noise: the spectrometer problem is different from network analyzer problem (Agilent example)**

Just because you have considered a 'THz' solution for your application and found it lacking does not mean that there is not a good SMM solution. Among THz technologies published in the 'best' journals there are orders of magnitude differences in the figures of merit that need to be selected according to application, especially:

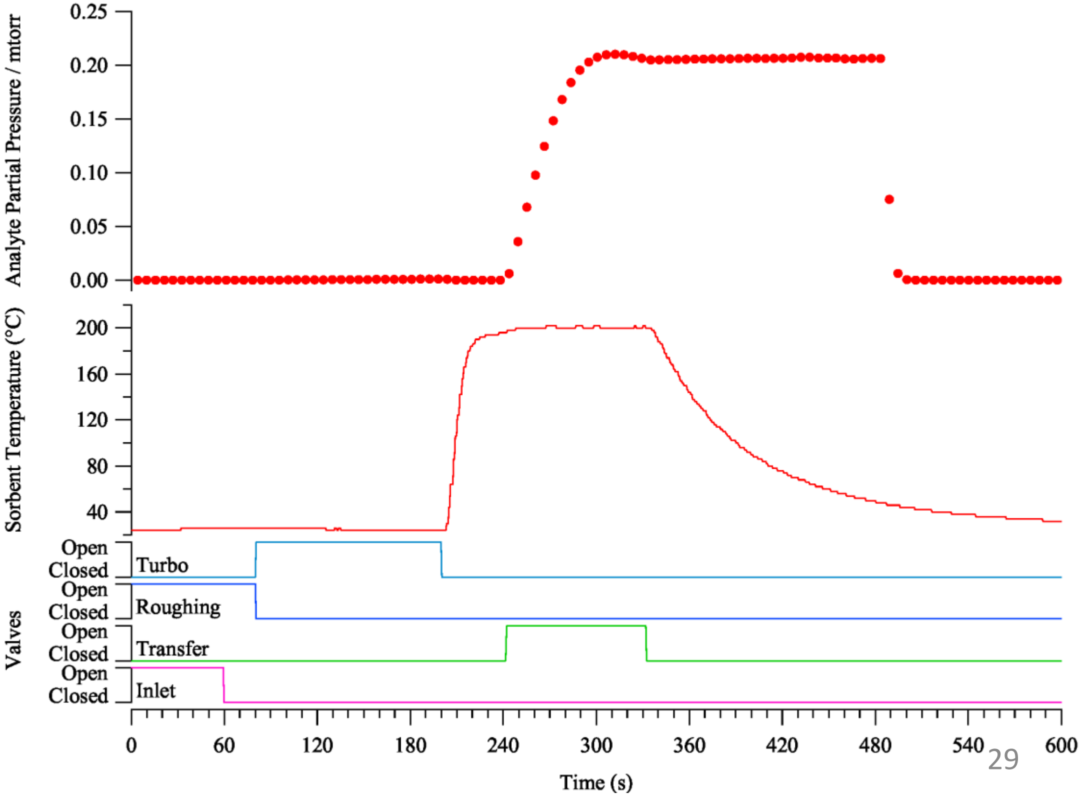
Brightness vs. 'dynamic range'
Resolution and frequency accuracy
Quality of implementation

There are also proposed 'THz' sensors that do not understand noise in the 'spectrometer problem' and propose (erroneously) many orders of magnitude better performance.

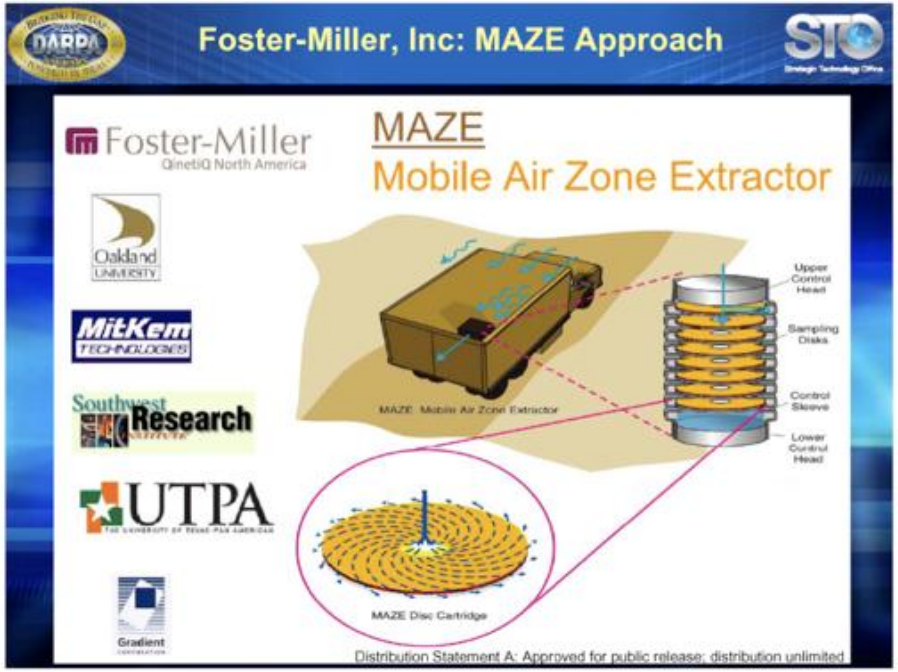
Sample Collection and Concentration

Large gains practical because we need very small (~10^{-5} STP liters), *static* samples.

MACS uses EPA/HAST like sorbent strategy to extend *beyond* the above comparisons.



DARPA gave us 10 minutes, so we used it. *Much* faster cycle times are possible.

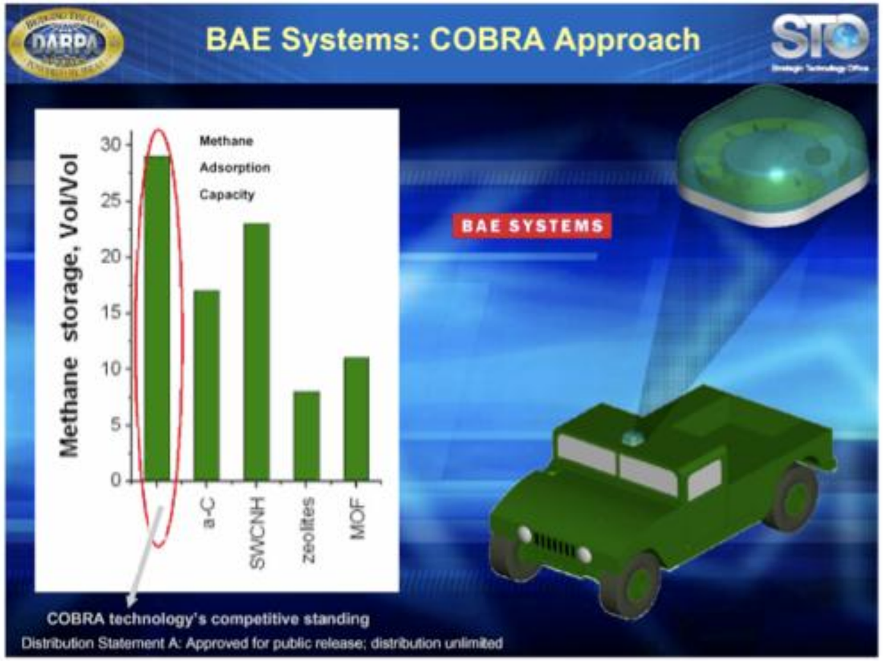


Foster-Miller, Inc: MAZE Approach

MAZE

Mobile Air Zone Extractor

Distribution Statement A: Approved for public release; distribution unlimited



BAE Systems: COBRA Approach

COBRA technology's competitive standing

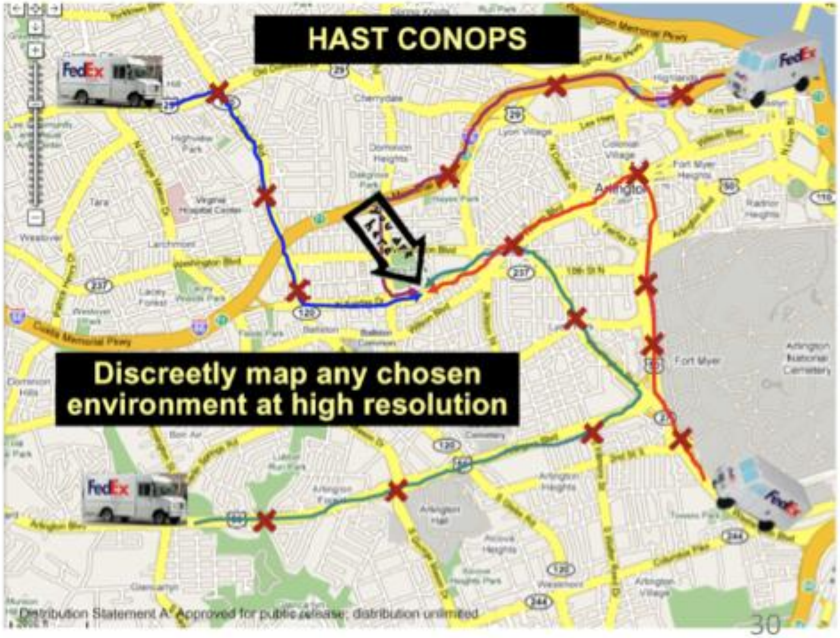
Distribution Statement A: Approved for public release; distribution unlimited

HAST Deployment

- Versatile Deployment on Mobile Platforms

Affixed on moving platform like a remora on a swimming shark, the HAST unit yields >100 composition measurements with better calibration and a smaller logistical tail.

Distribution Statement A: Approved for public release; distribution unlimited



HAST CONOPS

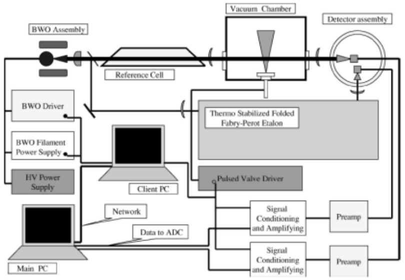
Discreetly map any chosen environment at high resolution

Distribution Statement A: Approved for public release; distribution unlimited

Paths Forward

[Time scales and Risks]

- More molecules
  - colder in beam systems
    - how do you count beam dilution?
  - stark
  - cavity
  - double resonance




JOURNAL OF CHEMICAL PHYSICS VOLUME 118, NUMBER 8 22 FEBRUARY 2003

The absorption spectroscopy of the lowest pseudorotational states of tetrahydrofuran

Dmitry G. Melnik, Sandhya Gopalakrishnan, and Terry A. Miller
Department of Chemistry, Ohio State University, Columbus, Ohio 43210

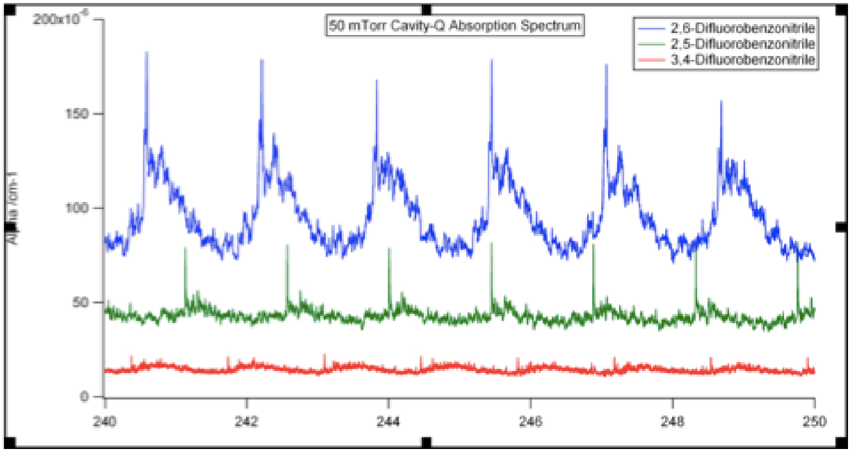
Frank C. De Lucia
Department of Physics, Ohio State University, Columbus, Ohio 43210

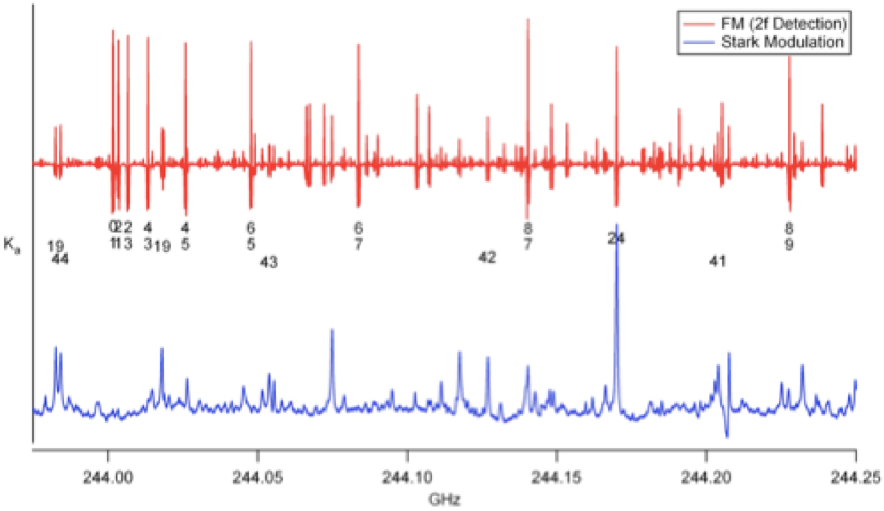
- Smaller, Cheaper, Lower Power
  - Both microwave and vacuum system matter
  - Less important for central systems like HAST

- Interaction of sample collection and spectroscopy
  - The ‘intricate dance’

- Adaptability (hardware, software, design) for special purposes
  - Larger for more sensitivity/speed

Cavity and Stark Approaches to Large Molecules



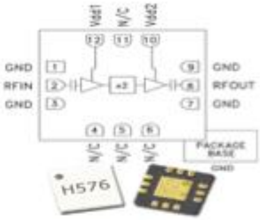


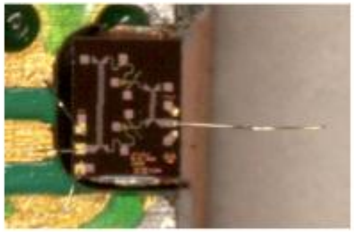
Cavity spectra of the difluorobenzonitriles.

A comparison of and FM modulate spectrum and a Stark modulated spectrum.

Clear Paths to Small and Inexpensive

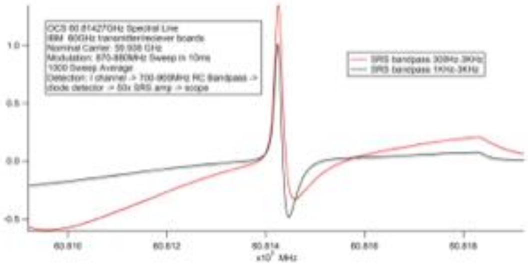
Wireless Communications chips to 100 GHz





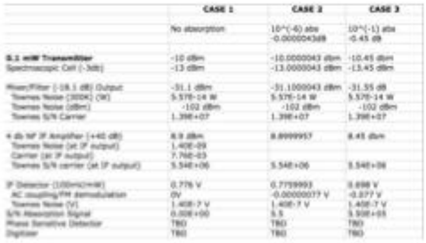
IBM 60 GHz Rx/Tx HDTV chip set working as spectrometer

discussions to extend to 100's of GHz

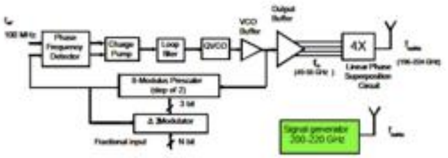


CMOS Integration of MACS Rx/Tx

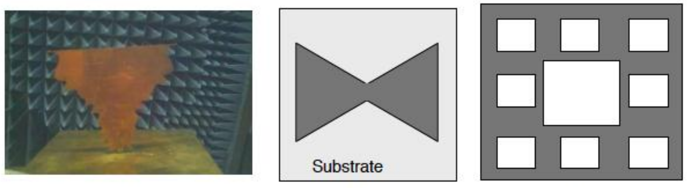
with UT-D and SRC sponsorship



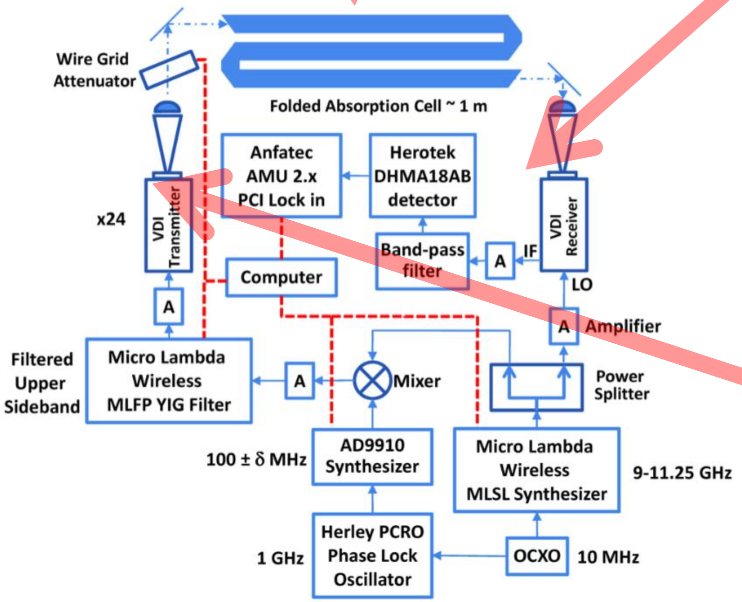
	CASE 1	CASE 2	CASE 3
	No absorption	10^(-6) abs -0.0000043dB	10^(-1) abs -0.45 dB
0.1 mW Transmitter	-10 dBm	-10.0000043 dBm	-10.45 dBm
Spectroscopic Cell (-3dB)	-13 dBm	-13.0000043 dBm	-13.45 dBm
Mixer/Filter (-18.1 dB) Output	-31.1 dBm	-31.1000043 dBm	-31.55 dB
Townes Noise (300K) (W)	5.57E-14 W	5.57E-14 W	5.57E-14 W
Townes Noise (dBm)	-102 dBm	-102 dBm	-102 dBm
Townes S/N Carrier	1.39E+07	1.39E+07	1.39E+07
4 db NF IF Amplifier (+40 dB)	8.9 dBm	8.8999957	8.45 dBm
Townes Noise (at IF output)	1.40E-09		
Carrier (at IF output)	7.76E-03		
Townes S/N carrier (at IF output)	5.54E+06	5.54E+06	5.54E+06
IF Detector (100mV/mW)	0.776 V	0.7759993	0.698 V
AC coupling/FM demodulation	0V	-0.00000077 V	-0.077 V
Townes Noise (V)	1.40E-7 V	1.40E-7 V	1.40E-7 V
S/N Absorption Signal	0.00E+00	5.5	5.50E+05
Phase Sensitive Detector	TBD	TBD	TBD
Digitizer	TBD	TBD	TBD

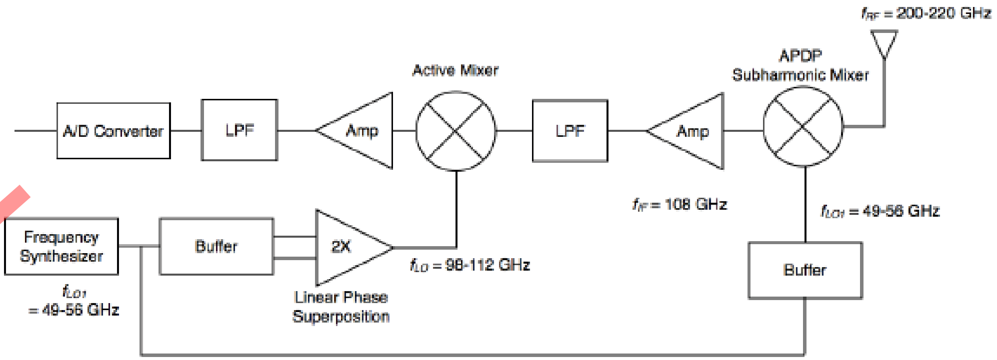


CMOS Integration for 240 GHz*

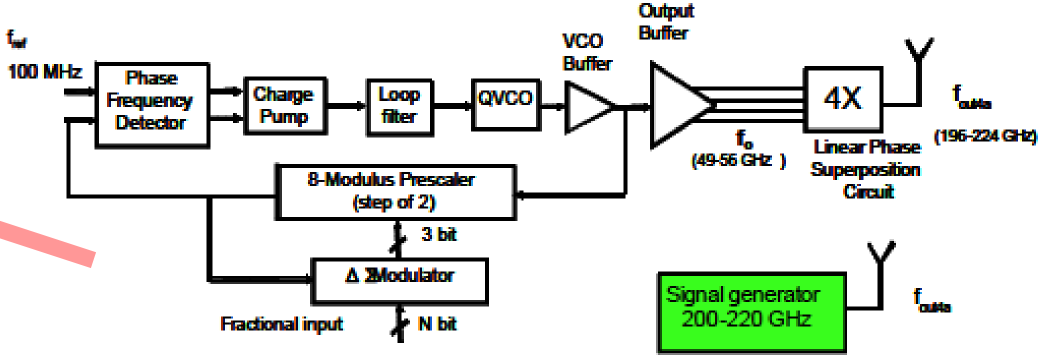


Antennas: Rashaunda Henderson (UT-D)





Receiver: Bhaskar Banerjee (UT-D)



Transmitter: Kenneth O (UT-D)

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*Sponsored by the Semiconductor Research Corporation

Point Sensor Summary

The current Phase I MACS is the brassboard of an operational sensor, with well defined capabilities as tested by a third party for DARPA.

The technology used has been shown to be fieldable.

There are a few, low risk upgrades which should be implemented, irregardless of application – can be done in the context of a brassboard system that would be prototype for production system.

It is likely that additional spectroscopy/library/preconcentration work will be required to meet specific needs of users.

There are well defined paths forward (often correlated with MACS Phase II) to meet a range of requirements.

Innovations and Advances to go beyond Current System Capabilities or Improve Technical/Physical Attributes

I. MM Technology
  A. Currently two VDI chains
  B. Move to one VDI, with double modulation
  C. 100 GHz Hittite system
  D. 250 GHz Wireless (Hittite?) system.
  E. CMOS system

II. X-band Technology
  A. Upgrade package current system
  B. Hittite Synthesizer(s)
  C. CMOS synthesizer(s)

III. Cells (alternatives and evolution)
  A. currently folded 1 m (0.5 liter)
  B. 0.3 m, 1 cm diameter (0.03 liter)
  C. 10 cm cavity (0.15 liter)
  D. 0.3 m, 1 mm diameter (0.0003 liter)
  E. Larger cell for optimized ppx sensitivity

IV. Pumps
  A. Currently, turbo + diaphragm
  B. Custom mechanical
  C. No pump

V. Sorbents
  A. Currently 3 cm x .5 cm cylinder
  B. Sandia-like micro hot plate (< 1 cm^3)
  C. Thermo cooler approaches
  D. Many other application dependent approaches

VI. Signal Recovery Technology
  A. Currently PC cage + lockin card + USB interface
  B. Laptop + custom lockin + USB interface
  C. Webbook + custom lockin + USB interface
  D. Custom, smart phone scale

VII. More and larger molecules
  A. Library development
  B. Sorbent/preconcentration development
  C. The intricate dance
  D. Cavity/medium resolution methods
  E. Stark modulation

Examples

(How the physics drives system choices)

Point Gas Sensors

Remote Gas Sensors

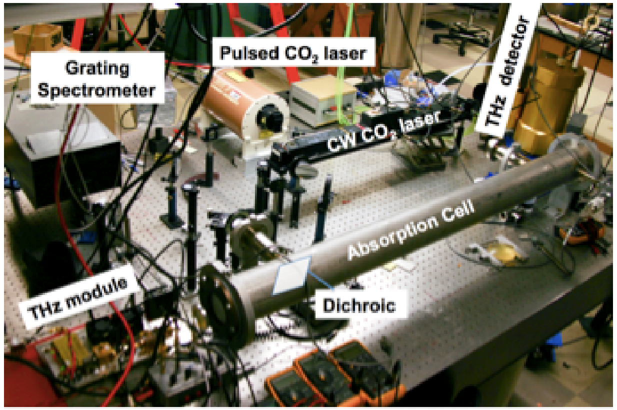
THz Imaging

New Physical Regime for Remote Sensing in the THz

PI: Frank De Lucia / Henry Everitt: Ohio State, AMRDEC
Award Number: HDTR1-09-1-0031

Objective: To develop fundamental understandings of collisional energy transfer in the high pump intensity – high pressure limit appropriate for highly specific atmospheric remote sensing.

Relevance: This project explores a fundamentally new concept for the remote detection of chemicals with specificity and sensitivity.



Approach: This project develops a general purpose double resonance energy transfer system for the study of energy transfer in the high intensity regime.

It also develops a comprehensive theoretical model.

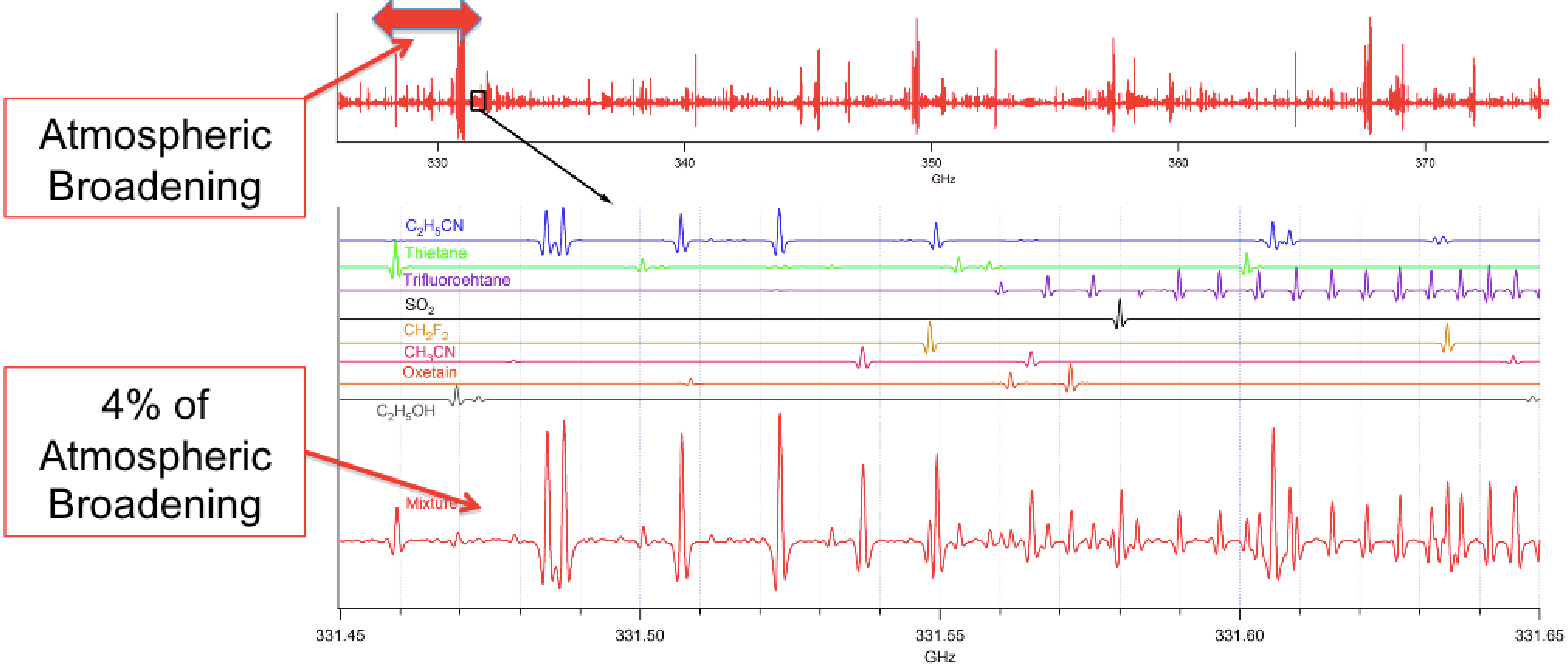
Both are applied to a range of molecular types.

Results:

Experimentally and theoretically explore:

3-D specificity matrix
Relation between signals at long and short time
Pump overlap as a function of pressure
Larger molecules with denser spectra

Low vs. High Pressure SMM/THz Spectroscopy



Atmospheric Broadening

4% of Atmospheric Broadening

A mixture of 20 gases – 'Absolute' specificity at low pressure (10^{-5} atm)
3 seconds of data acquisition => information graph 100 m x 1 km

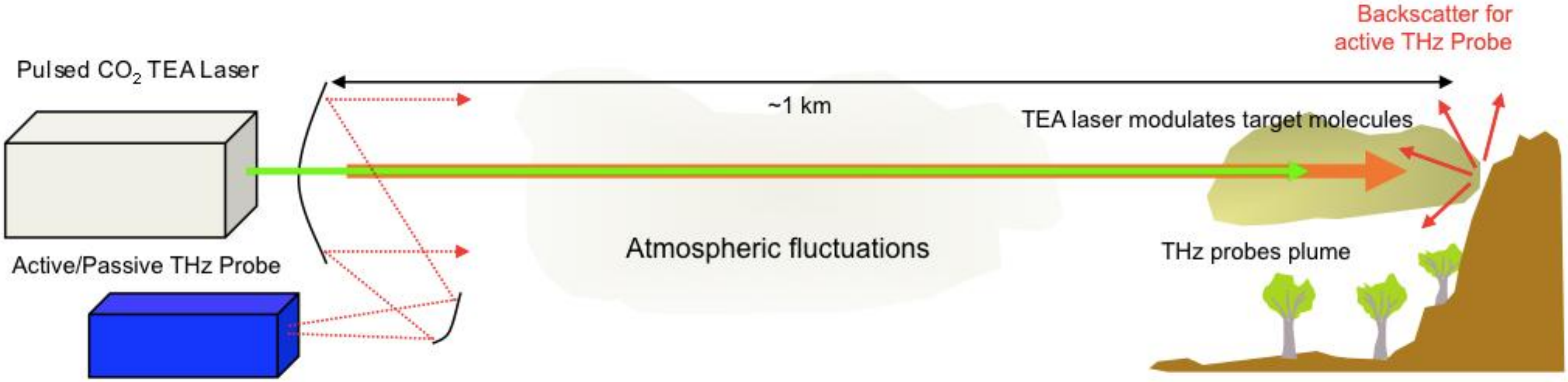
At atmospheric pressure fingerprint lines 10^4 broader (~5000 MHz)

- **Specificity: 5000 times fewer resolution elements**
- **Orders of magnitude reduction in sensitivity because of ~10% baseline problem**

These challenges are easy to ignore: Doesn't impact ideal sensitivity calculations

Very special favorable cases can be chosen to eliminate specificity problems

A Solution: A New Physical Regime via Double Resonance



Problem # 1: Specificity

Dimension 1: Choose IR pump frequency

Dimension 2: Monitor the SMM/THz probe frequencies

Dimension 3: Match pump pulse to relaxation of atmosphere (~100 ps)

=> Large number of points in 3-D space increases specificity

=> Time dimension measure of environmental interactions

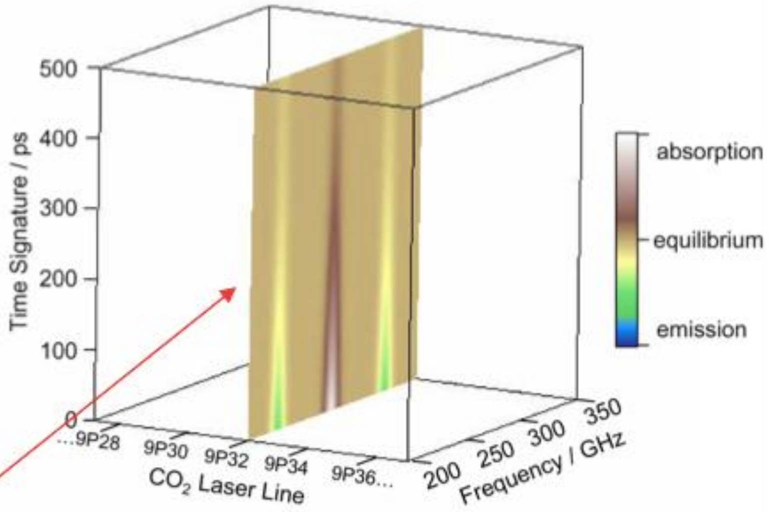
=> Different slices are measures of different interactions

Problem # 2: Separation of target signature from baseline and clutter

Lock on to IR pulse sequence to reject atmospheric clutter -

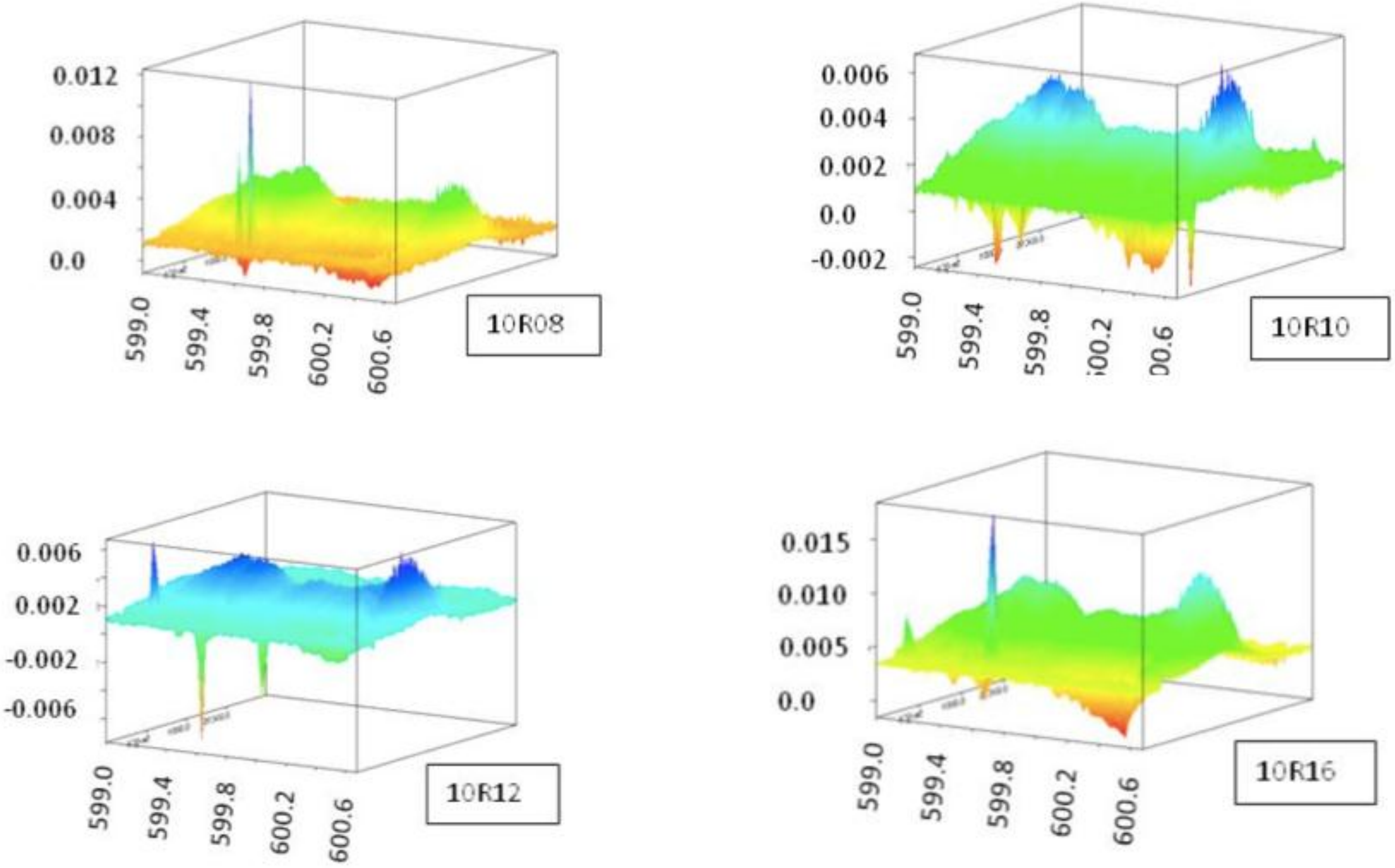
=> Elimination of 10% baseline effect increases sensitivity by 10^6

3-D Specificity Cube



Probe slice for a *particular* pump

3-D Signatures



Double resonance signatures of 1,1,1 trifluroethane for four different laser pumps.

Double Resonance Paths Forward

Atmospheric Remote Sensing

Signatures and physics in the high pump (fixed frequency), high pressure, 100 ps regime

DARPA funded laser under construction

Large Molecules in Point Sensors

Signatures in the ns regime
Operate at reduced pressure
Smaller QCL lasers (tunable)

Examples

(How the physics drives system choices)

Point Gas Sensors

Remote Gas Sensors

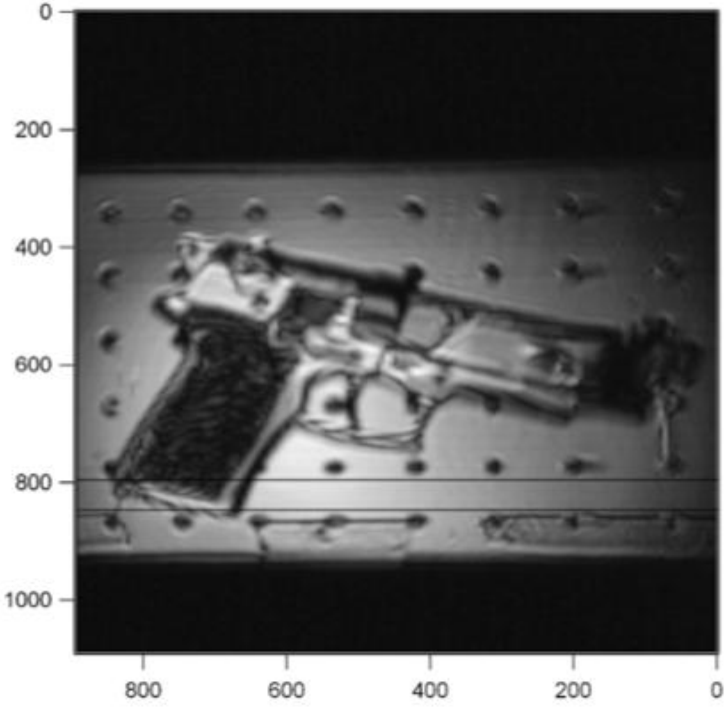
THz Imaging

Active Imaging without Coherent Speckle or Special Angle Requirements:

Modulated Mode Mixing

"Passive" Cold sky illumination at 0.094 THz

Specular target at special angle => strong return, no speckle



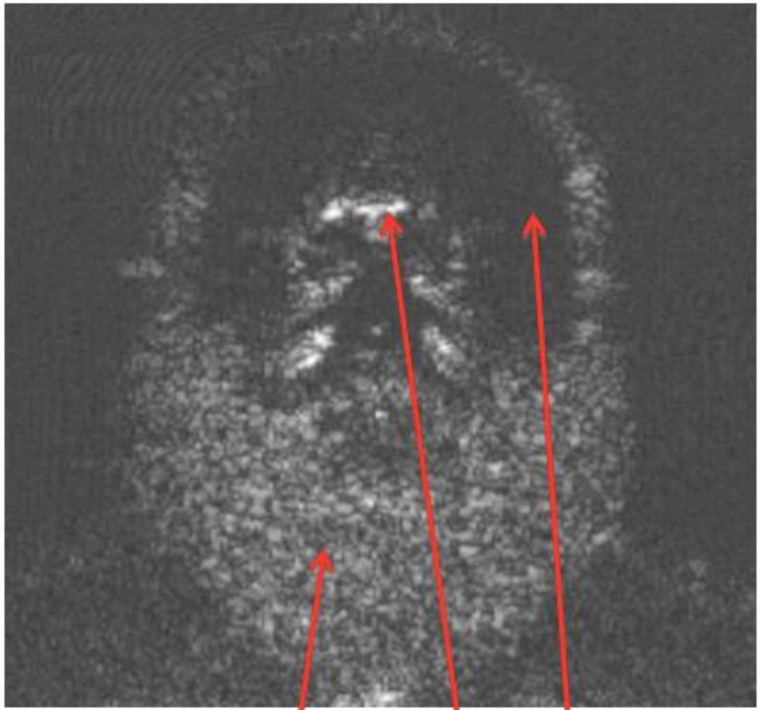
Angle and Coherent Effects in Active Images

Passive Image

No Speckle

No orientation requirements

Active Image



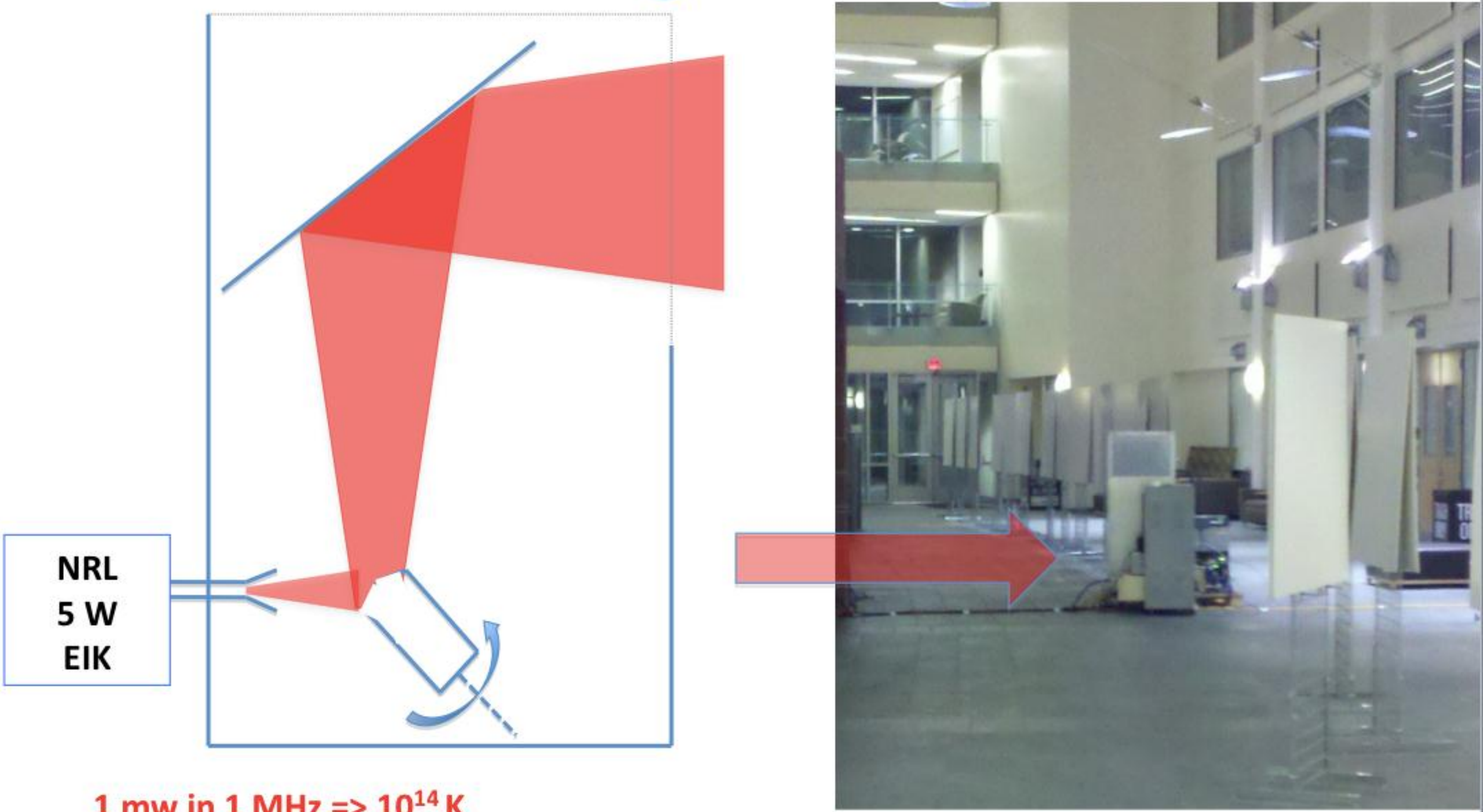
Speckle

Normal orientation

Non-normal orientation

Goal: Use M^3 to produce *very* hot (1 mw in 1 MHz => 10^{14} K) incoherent black body

218.4 GHz Imager in Large Volume



1 mw in 1 MHz => 10^{14} K

Vacuum electronics makes possible very hot multimode illumination in atrium and extension to considerably greater range (~1 km)

Physics Atrium as 50 Meter Range

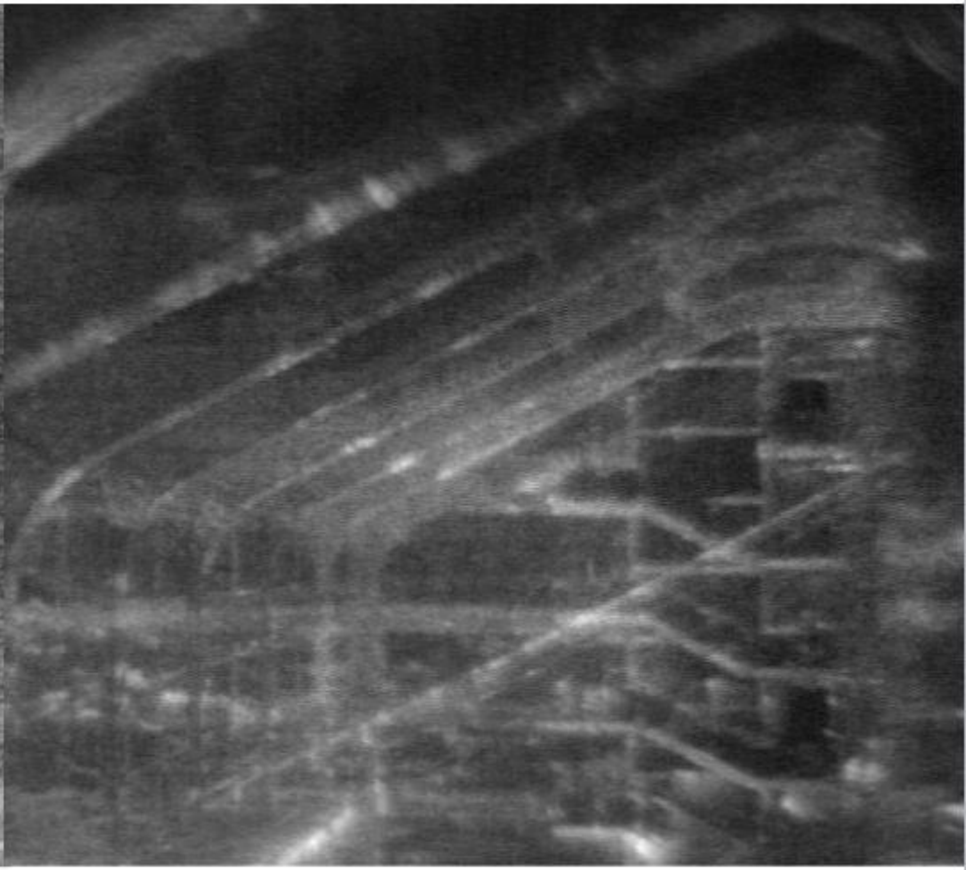
Optical Image

**217 GHz Image
(without mode modulation)**

Speckle => 100% noise modulation on image
=> cannot take advantage of illumination power

Modulated Multimode Mixing

217 GHz Image
(without mode modulation)



217 GHz Image
(with mode modulation)

Summary and Comments

There are clear development paths to important applications (match scenario to capability).

There are clear R&D paths to broaden ‘read to go’ capabilities.

There are many orders of magnitude at stake in the evaluation of proposed THz applications, often as steep functions of frequency.

The choice of technology also has many orders of magnitude impact.

Special selection of illumination in imaging and molecule selection in spectroscopic sensors in demonstrations also are orders of magnitude effects.

Quantitative analyses (many of which can be done quite simply) are required to select promising applications and the appropriate technology to support them.

We have developed:

1. A gas sensor capable of analysis of complex mixtures of gases. Need to follow the clear paths to small and inexpensive systems. R&D to broaden applicability.

2. A double resonance scheme for atmospheric remote sensing/large molecule detection. Need to evaluate target signatures in operational pulse regimes.

3. An active imaging approach which eliminates the need for special target orientation and coherent effects such as speckle; effectively producing very hot, passive-like images. More generally, need to explore phenomenology, illumination strategies, longer ranges, and system implementations.

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