Department of Physics
Microwave Laboratory

Point and Remote Chemical Sensors in the Millimeter and Submillimeter Spectral Region

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URSI
Boulder
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Millimeter and Submillimeter (MM/SUBMM) Gas Sensors

There are widely publicized

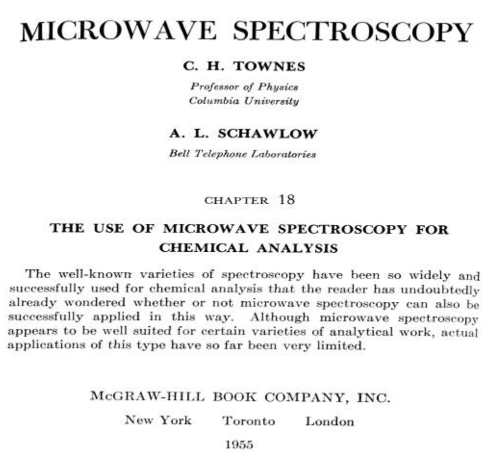
Optically based Terahertz (THz) gas sensors

Infrared and optical gas sensors

Will show today that the electronic technology familiar to those in attendance here is VERY competitive

Gas Analysis Emerges from a Confluence of Science and Technology

Physics Always Favorable (1955)


MICROWAVE SPECTROSCOPY

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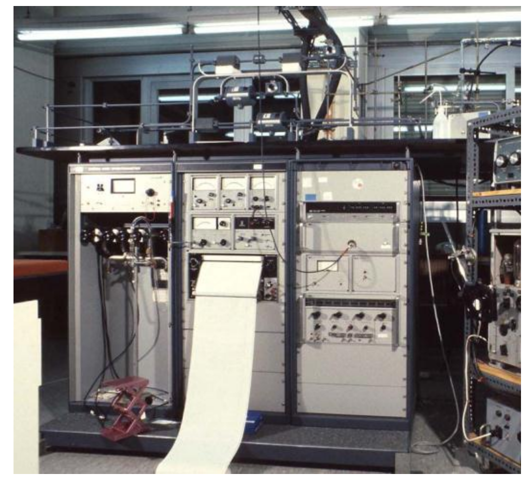
CHAPTER 18

THE USE OF MICROWAVE SPECTROSCOPY FOR CHEMICAL ANALYSIS

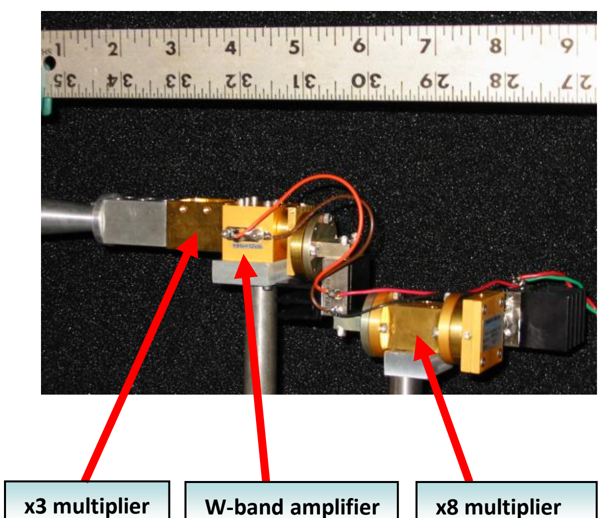
The well-known varieties of spectroscopy have been so widely and successfully used for chemical analysis that the reader has undoubtedly already wondered whether or not microwave spectroscopy can also be successfully applied in this way. Although microwave spectroscopy appears to be well suited for certain varieties of analytical work, actual applications of this type have so far been very limited.

McGRAW-HILL BOOK COMPANY, INC.
New York Toronto London
1955

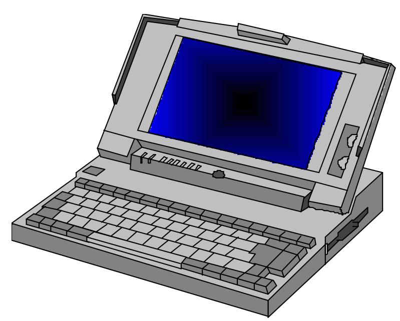
HP 40 GHz MW Spectrometer(1974)



Microfabrication => small, inexpensive in quantity



Enablers



Growth in computing power to handle information

Broadband wireless market

CMOS

Spectroscopic and Analytical Background

A Fast Scan Submillimeter Spectroscopic Technique, **Rev. Scient. Instrum. 68, 1675-1683 (1997).**

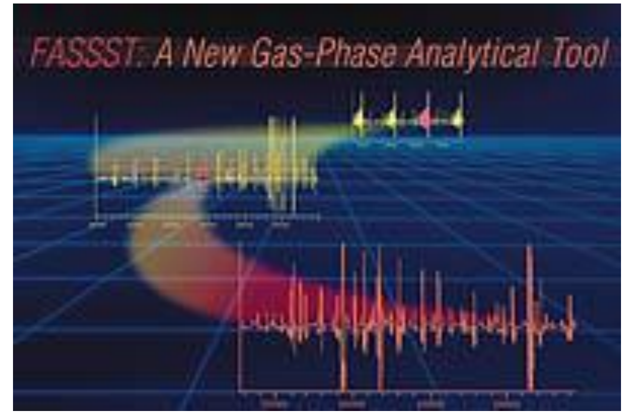
FASSST: A new Gas-Phase Analytical Tool**, Anal. Chem. 70, 719A-727A (1998).**

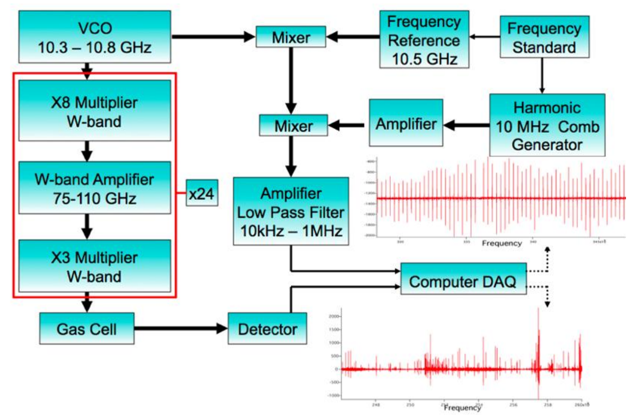
Fast analysis of gases in the submillimeter/terahertz with "absolute" specificity, **Appl. Phys. Lett. 86, 154105 (2005).**

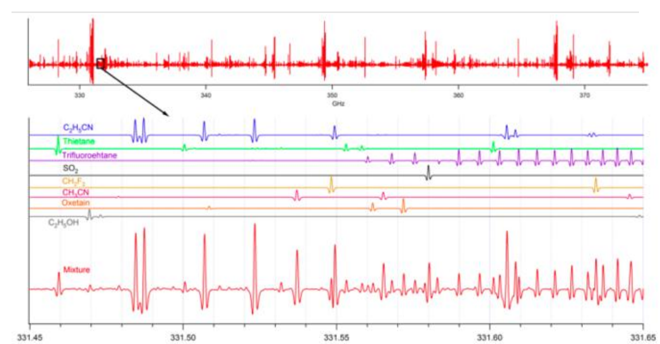
Chemical analysis in the submillimeter spectral region with a compact solid state system, **Analyst 131, 1299-1307 (2006).**

A new approach to astrophysical spectra: The complete experimental spectrum of ethyl cyanide (CH_3CH_2CN) between 570 and 645 GHz, **Ap. J. 713, 476 (2010).**

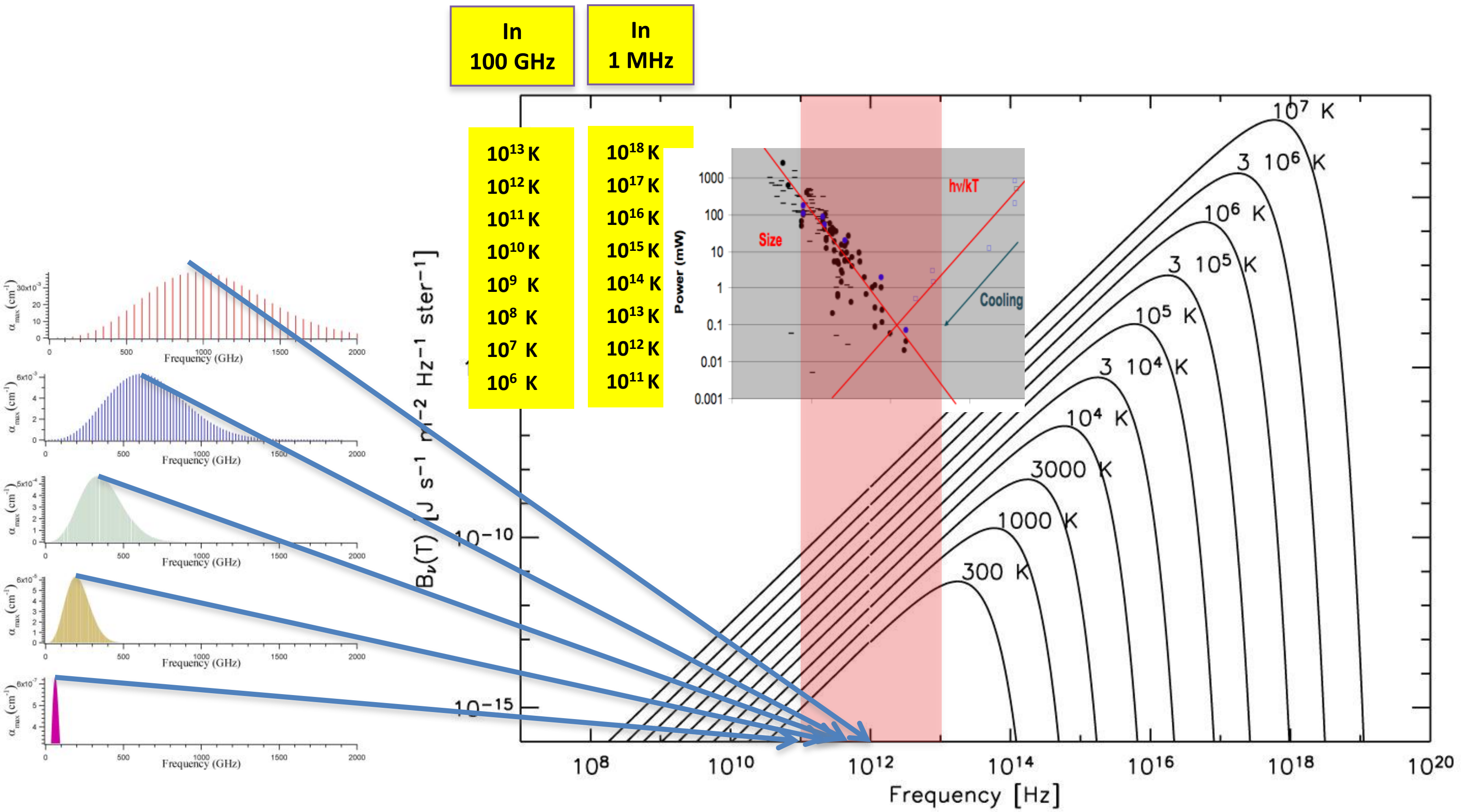
Submillimeter spectroscopy for chemical analysis with absolute specificity, I. R. Medvdev, C. F. Neese, G. M. Plummer, and F. C. De Lucia, **Opt. Lett. 55, 1533 (2010).**







Radiation and Interactions: Orders of Magnitude



The SMM/THz – broadly defined

Jumping the 'gap in the electromagnetic spectrum' is not the same as closing it

Bandwidth matters: Spectral Brightness and Figures of Merit

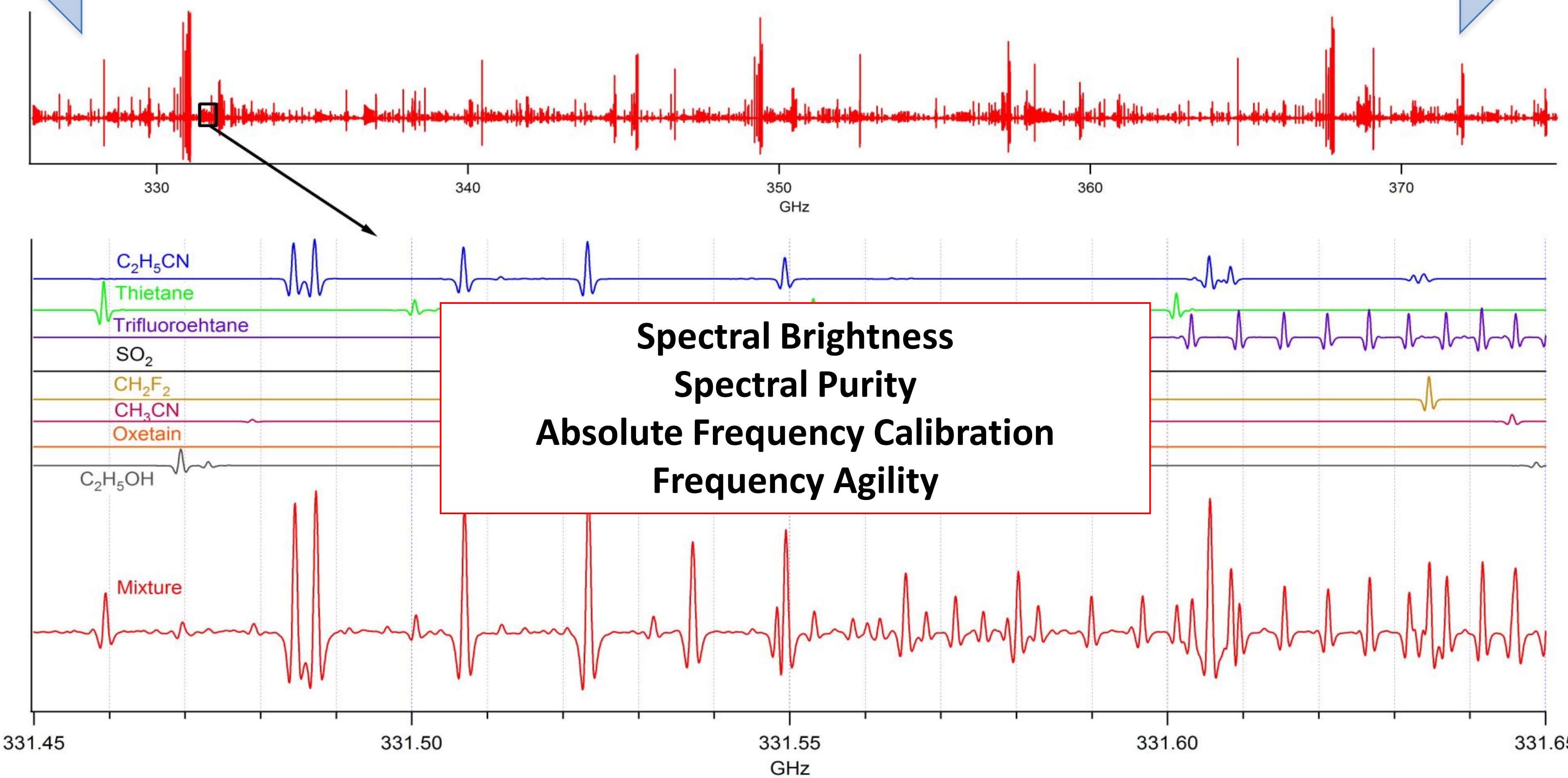
Spectral distribution as function of molecular size at 300 K

For samples in thermal equilibrium, Doppler broadening is proportional to frequency

SMM and small static samples are favorable combination

Spectrum of a Mixture of 20 Gases

Three seconds of data acquisition expands to 1 kilometer at scale of lower panel



Broad Coverage of TIC Gases

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

HCl

Chemical	Rate of Onset	Persists in Environment	Toxicity Thresholds (ppm/hour) impairment	fatality	BDO/ Mask Effective	Odor	Related hazards/ Source/ Use	Field Detection: Sensidyne tube (#)	Field Detection: 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)
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

Symptoms *(from inhalation and dermal contact)*

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 and Treatment

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 →

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) impairment / fatality	BDO/ Mask Effective	Odor	Source/ Use/other hazard	Field Detection: Sensidyne tube (#)	Field Detection: 205Aseries Miran SapphiRE	Symptoms (from inhalation and dermal contact)	Decontamination and Treatment
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	<u>General Mild Health Effects:</u> - Nausea, dizziness; headaches; chills; coughing, choking, throat irritation <u>Specific and More Severe Effects:</u> *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) <u>Additional Chemical Specific Symptoms:</u> *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	<u>Decontamination:</u> - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse <u>Treatment & Diagnostic procedures/ options:</u> *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)		

Low Atmospheric Clutter Background

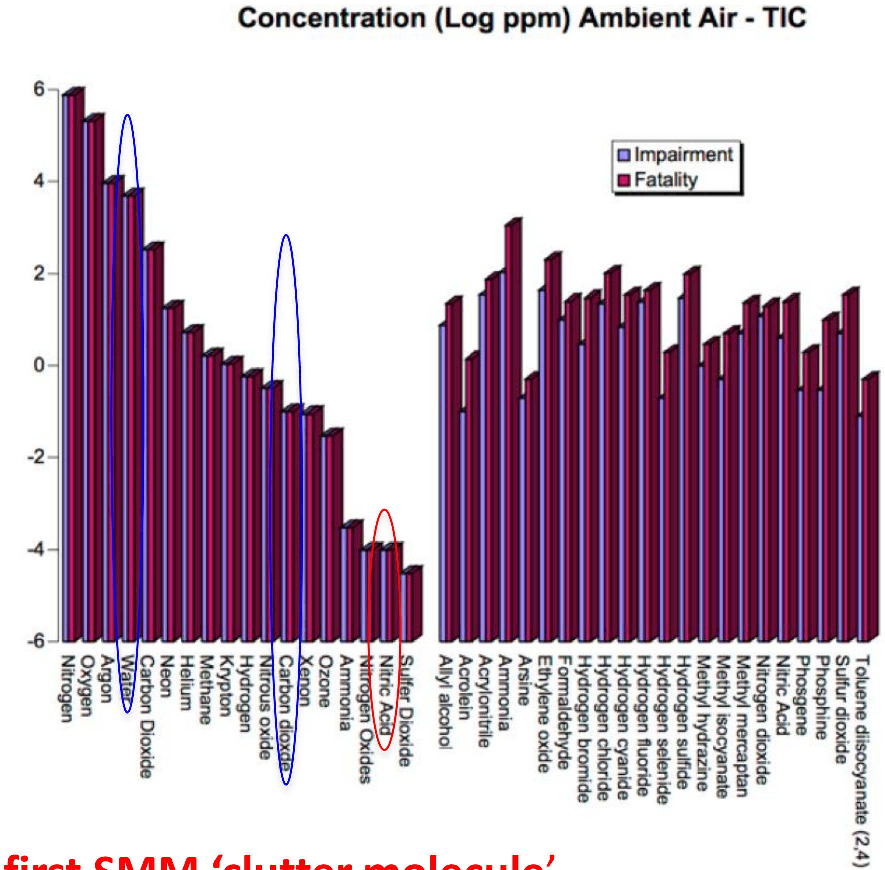
[The miracle of the SMM]

Table III.1 Molecular Concentrations in the Clean Troposphere and the Polluted Urban Air (ppb).[*]

Species	Clean Troposphere	Polluted Air
N_2	780,840,000	780,840,000
O_2	209,460,000	209,460,000
H_2O	variable	variable
Ar	9,340,000	9,340,000
Ne	18,000	18,000
He	5200	5200
Kr	1100	1100
Xe	90	90
H_2	580	580
CH_4	1650	1650+
CO_2	332000	332000+
N_2O	330	330+
SO_2	1 – 10	20 – 200
CO	120	1000 – 10000
NO	0.01 – 0.05	50 – 750
NO_2	0.1 – 0.5	50 – 250
O_3	20 – 80	100 – 500
HNO_3	0.02- 0.3	3 – 50
NH_3	1	10 – 25
H_2CO	0.4	20 – 50
HCOOH		1 – 10
HNO_2	0.001	1 – 8
$CH_3C(O)O_2NO_2$ (PAN)		5 – 35
Non-Methane Hydrocarbons		500 – 1200

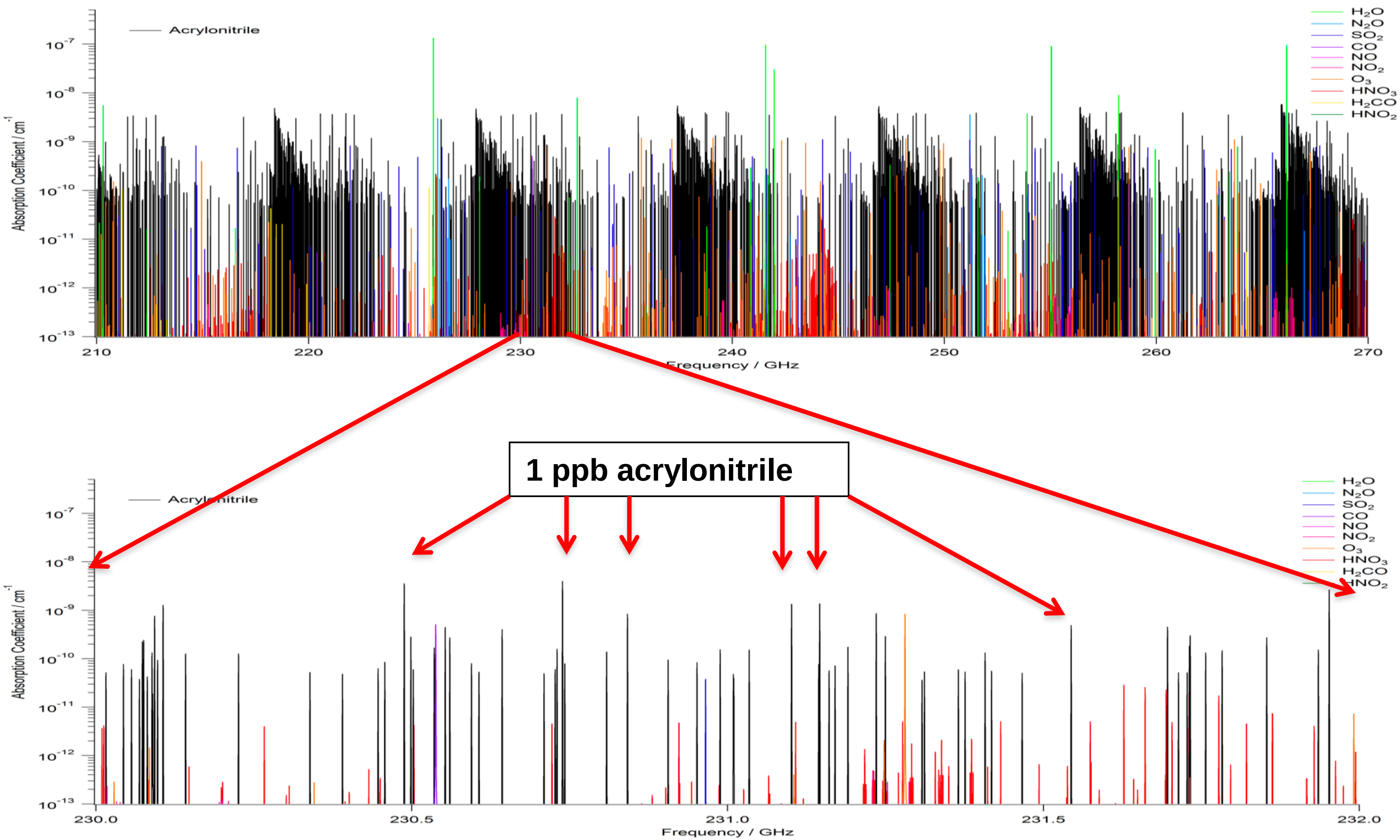
[*].Data from Seinfeld[4]

Major Infrared Clutter



Nitric acid at ~ 1ppb is first SMM 'clutter molecule'

1 ppb Acrylonitrile in Atmospheric Clutter*



Detailed simulations show that the SMM clutter limit is around 1 ppt *without* preselection

*** I. R. Medvedev, C. F. Neese, G. M. Plummer, F. C. De Lucia, Applied Optics 50, 3028 (2011)**

Sensor and Analysis Trade Space

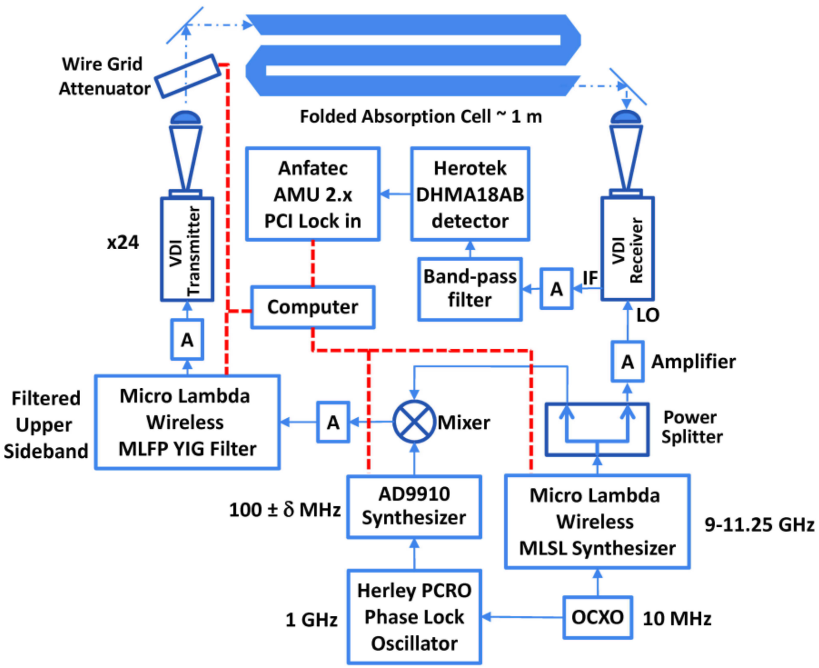
- Very complicated for spectroscopic sensors

- First: Show particular optimization
- Second: Consider trades from this locus

- Trades
  - Speed
  - Sensitivity
  - Specificity
  - Generality
  - Size – Cost

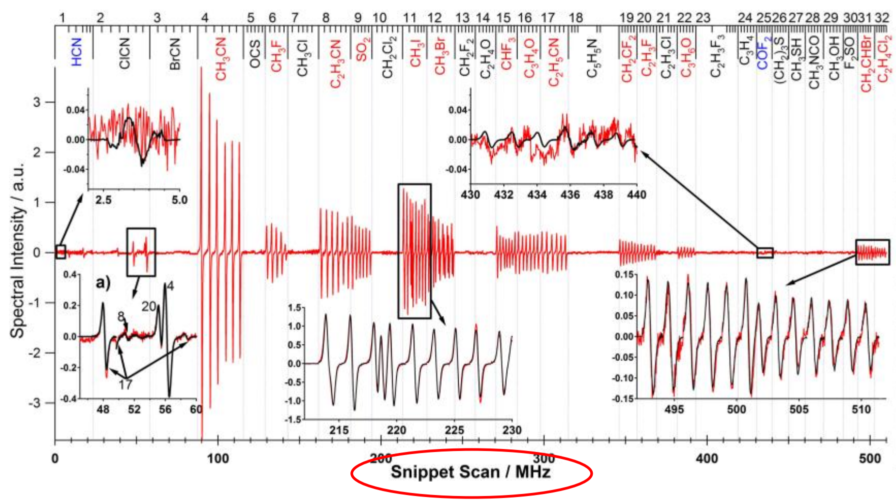
An Implementation as a Point in Trade Space

Goals:
1 Cubic Foot Self-contained Box
$<10^{-4}$ PFA on >30 gas mixture
<100 ppt on one gas



Synthesized snippets to optimize photon use

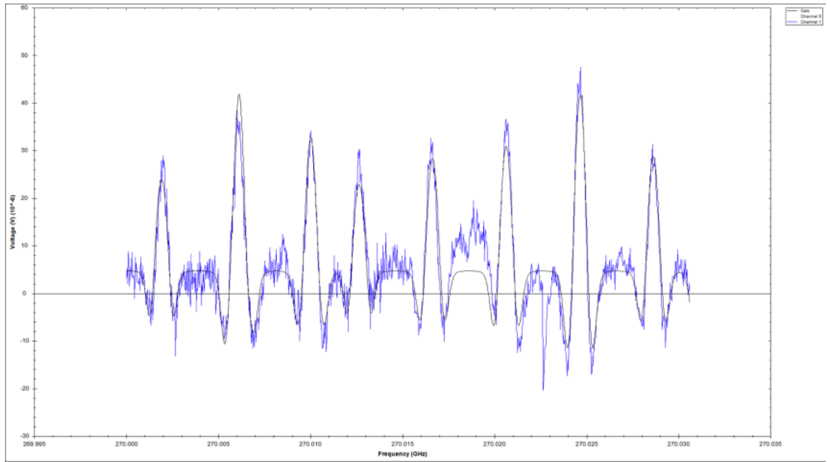
'absolute' specificity on mixture of 32



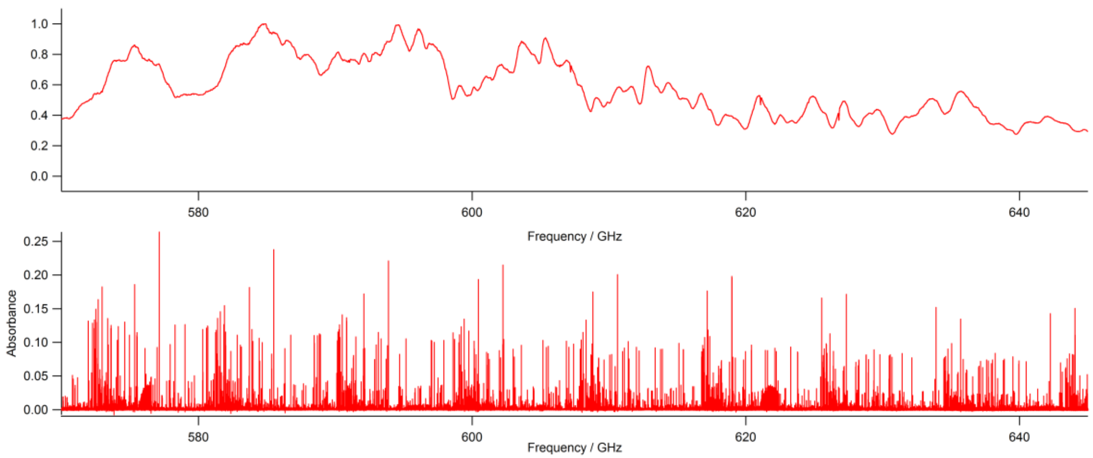
	Pressure /μtorr	S/N
1	0.06	5.0
2	0.00	0.4
3	0.02	1.3
4	61.79	598.2
5	-0.02	0.5
6	26.97	304.7
7	0.00	0.1
8	66.09	432.5
9	54.13	323.8
10	0.12	1.2
11	130.10	404.2
12	85.04	390.4
13	0.16	1.0
14	-0.02	0.1
15	70.05	273.0
16	58.93	281.2
17	60.61	321.7
18	-0.12	0.8
19	55.67	192.8
20	40.31	161.3
21	-0.55	2.0
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

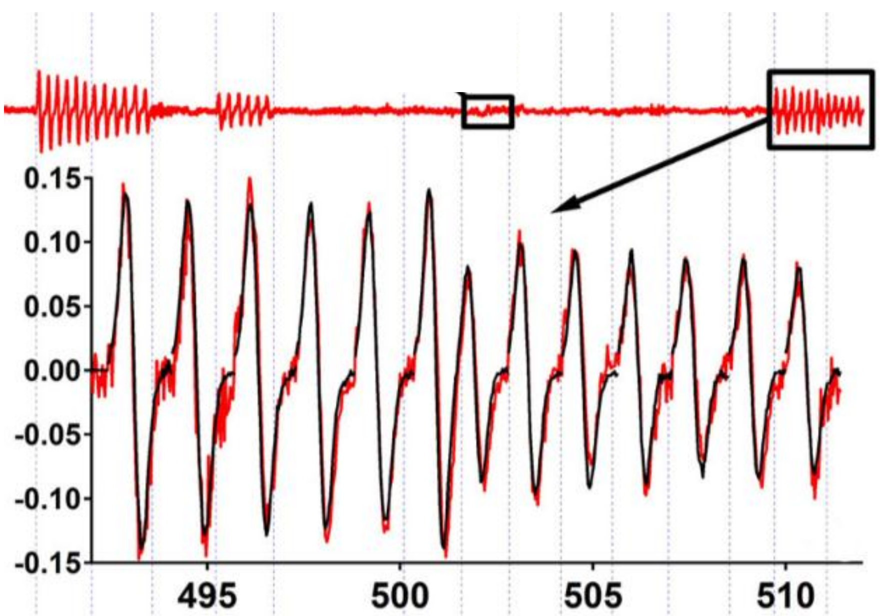
∑ = 0.89 mtorr

2 ppt sensitivity demonstrated on one gas



Intensity Calibration

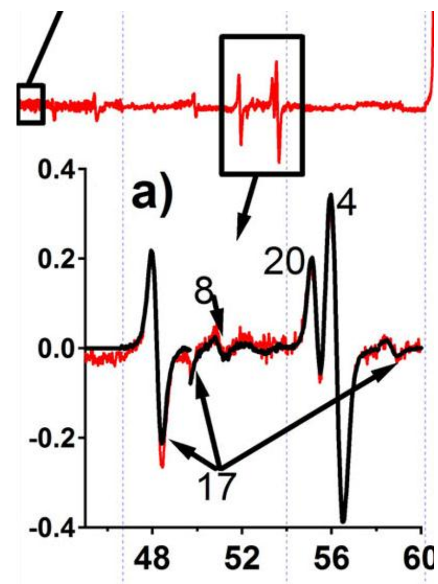




CH_2CHBr / $C_2H_4Cl_2$ Snippets

Subtraction of spectra due to four other species in ClCN snippets

Requires overlapping gases be in library



ClCN Snippets

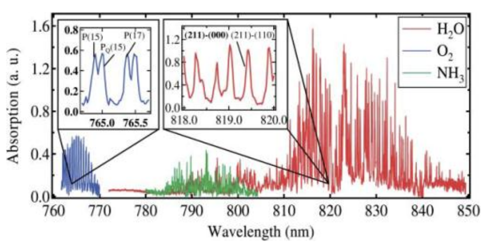
Results of Numerical Analysis

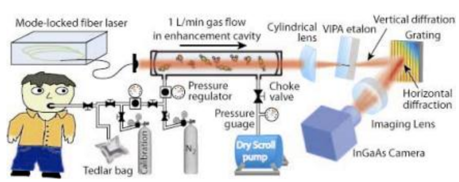
	Name	Partial Pressure	Uncertainty	σ
1	Hydrogen Cyanide (HCN)	0.00005887	0.00001177	5.0
2	Cyanogen Chloride (ClCN)	0.00000373	0.00000863	0.4
3	Cyanogen Bromide (BrCN)	0.00001529	0.00001190	1.3
4	Acetonitrile (CH_3CN)	0.06179212	0.00010329	598.2
5	Carbonyl Sulfide (OCS)	-0.00002180	0.00004785	0.5
6	Methyl Fluoride (CH_3F)	0.02696802	0.00008850	304.7
7	Methyl Chloride (CH_3Cl)	0.00000402	0.00006642	0.1
8	Acrylonitrile (C_2H_3CN)	0.06608506	0.00015278	432.5
9	Sulfur Dioxide (SO_2)	0.05412899	0.00016715	323.8
10	Dichloromethane (CH_2Cl_2)	0.00011741	0.00009868	1.2
11	Methyl Iodide (CH_3I)	0.13009995	0.00032185	404.2
12	Methyl Bromide (CH_3Br)	0.08504046	0.00021784	390.4
13	Difluoromethane (CH_2F_2)	0.00015923	0.00015236	1.0
14	Ethylene Oxide (C_2H_4O)	-0.00002183	0.00016894	0.1
15	Trifluoromethane (CHF_3)	0.07005161	0.00025661	273.0
16	Acrolein (C_3H_4O)	0.05893068	0.00020953	281.2
17	Propionitrile (C_2H_5CN)	0.06061219	0.00018844	321.7
18	Pyridine (C_5H_5N)	-0.00011725	0.00014392	0.8
19	1,1 Difluoroethene (CH_2CF_2)	0.05567078	0.00028872	192.8
20	Vinyl Fluoride (C_2H_3F)	0.04030862	0.00024987	161.3
21	Vinyl Chloride (C_2H_3Cl)	-0.00055029	0.00027035	2.0
22	Oxetane (C_3H_6O)	0.03009420	0.00032445	92.8
23	1,1,1 Trifluoroethane ($C_2H_3F_3$)	-0.00007049	0.00021531	0.3
24	Propyne (C_3H_4)	-0.00016353	0.00034151	0.5
25	Carbonyl Fluoride (COF_2)	0.00467462	0.00048952	9.5
26	Thietane ($(CH_2)_3S$)	-0.00089690	0.00049489	1.8
27	Methyl mercaptan (CH_3SH)	0.00009574	0.00060512	0.2
28	Methyl isocyanate (CH_3NCO)	0.00080489	0.00052955	1.5
29	Methanol (CH_3OH)	0.00026869	0.00046662	0.6
30	Thionyl fluoride (F_2SO)	-0.00063312	0.00058645	1.1
31	Vinyl bromide (CH_2CHBr)	0.07177855	0.00058255	123.2
32	1,2 dichloroethane ($C_2H_4Cl_2$)	0.07311919	0.00088521	82.6
		∑ = 0.888408		

DARPA Requested Comparisons

	Optical Comb/Cavity 100 Torr[1]	SMM 1.5 m Cell 10 mTorr	THz-TDS 5 m White Cell 7.5 mTorr[2]
$\Delta\nu_{system}$	1600 MHz	0.5 MHz	3000 MHz
$\Delta\nu_{instrument}$	800 MHz	0.001 MHz	3000 MHz
NH_3	18 ppb $9.6\text{x}10^{-11}$ mole	52 ppb $2.7\ \text{x}10^{-14}$ mole	---
CO	900 ppb $4.8\text{x}10^{-9}$ mole	280 ppb $1.5\ \text{x}10^{-13}$ mole	---
HCN	---	10 ppb $5.3\ \text{x}10^{-15}$ mole	---
CH_3CN	---	50 ppb $2.7\ \text{x}10^{-14}$ mole	---
CH_3Cl	---	---	$10^9/10^4$ ppb[5] $4\ \text{x}\ 10^{-7}/10^{-12}$ mole

• Entire system is contained within 8 cubic feet.
• Subsystems include two lasers, photomixers, control electronics, and sample cell.
• THz output tunable from 100 GHz to 1.4 THz with 1.1 MHz resolution





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-TDS:

- has $>10^3$ less ppx sensitivity
- requires 10^6 more sample – sorbent difficult
- has $>10^4$ lower resolution
- very sensitive to water interference
- somewhat 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)

Comparison Requested by IEEE Sensors

A Comparison with an Optical THz Sensor

	This Work	Ref. [1]	Ratio
Source Width	0.01 MHz	11000 MHz	~10^6
Frequency Accuracy	~0.01 MHz	~5000 MHz	~10^6
Measurement time/pt	0.01s	60	6000
Signal/Noise (Opt pressure)	~50000	~10	5000
Working Pressure	0.0001 Torr	100 Torr	10^6
Optimum Pressure	0.01 Torr	100 Torr	10^4
Sensitivity (ppx normalized)	3 x 10^5	1	3 x 10^5
Sensitivity (mole normalized)	3 x 10^9	1	3 x 10^9

H. Sun, Y. J. Ding, and I. B. Zotova, "THz Spectroscopy by Frequency-Tuning Monochromatic THz Source: From Single Species to Gas Mixtures," *IEEE Sensors*, Vol. 10, pp. 621-629, 2010.

How Can This Be?

The Physics is very favorable for electronic sensors in the MM/SUBMM

Source brightness of ~10^{14} K
Synthesized frequency agility
Rotational matrix elements >> Vibrational matrix elements
Doppler width proportional to frequency
Absorption strength goes as ν^3 - peaking at ~0.2 – 1 THz
The 1 ppt atmospheric clutter 'miracle'

How Can the Literature Be So Unaware?

From Optical Society of America

Toronto, June 2011

Department of Physics
Microwave Laboratory

The Three Cultures*

THZ/Optical

Optical Society of America,
"THz Spectroscopy and Imaging Applications"
Toronto, June 14, 2011

Millimeter/Electronic (Engineering)

IEEE International Microwave Show 2011
"Workshop on MM-Wave and Terahertz Systems"
Baltimore, MD, June 6, 2011

Submillimeter/Electronic (Scientific)

International Astronomical Union,
"The Molecular Universe"
Toledo Spain, June 2, 2011

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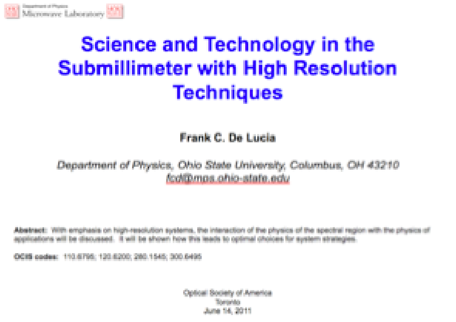
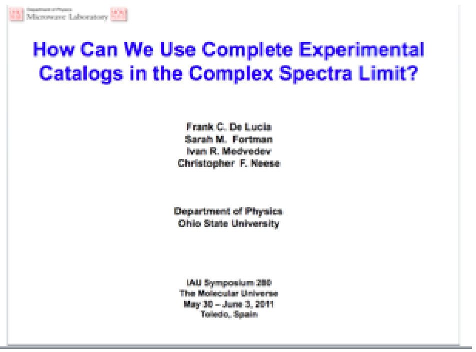
*With apologies to C. P. Snow, "The Two Cultures"





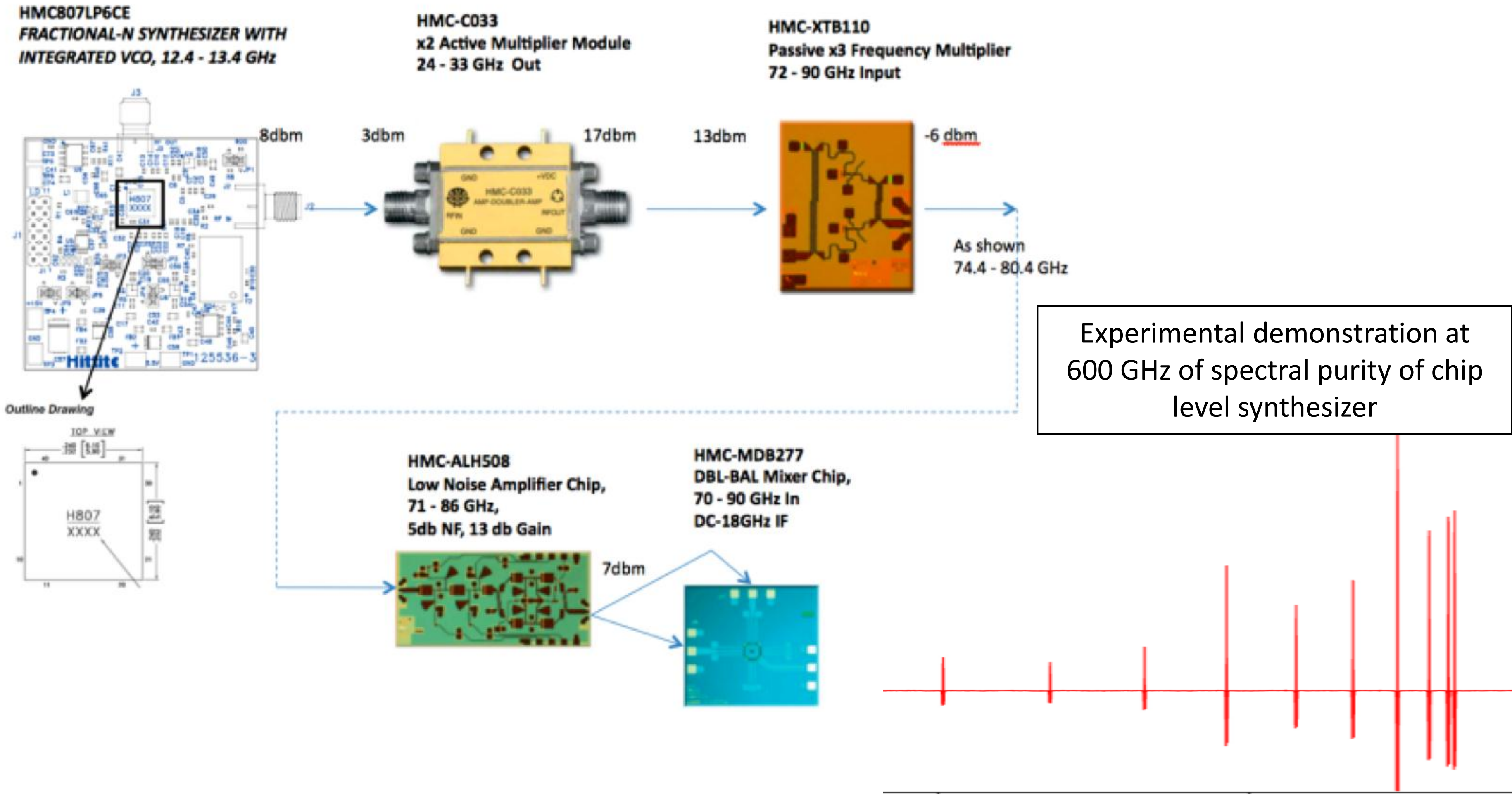
The Really Good News for Electronic Technologies:

Advances in Electronic Technology

Size and Cost Drivers from the Wireless Communications Industry

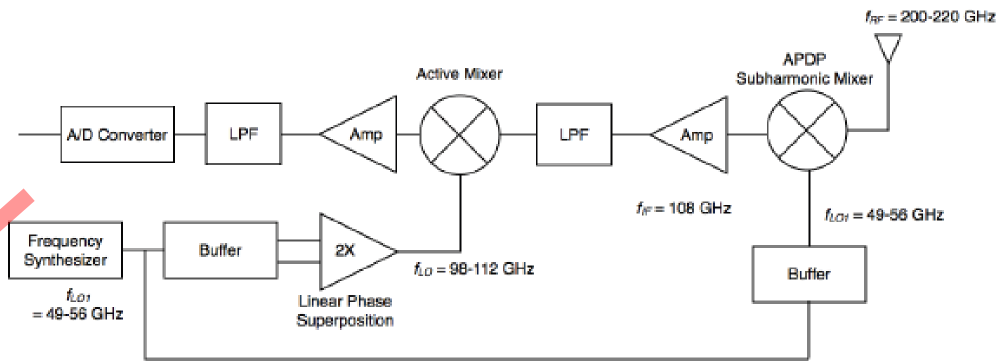
Because the brightness of low power, high spectral purity sources is very high the ‘physics’ to support low cost, small size, and low power is very favorable

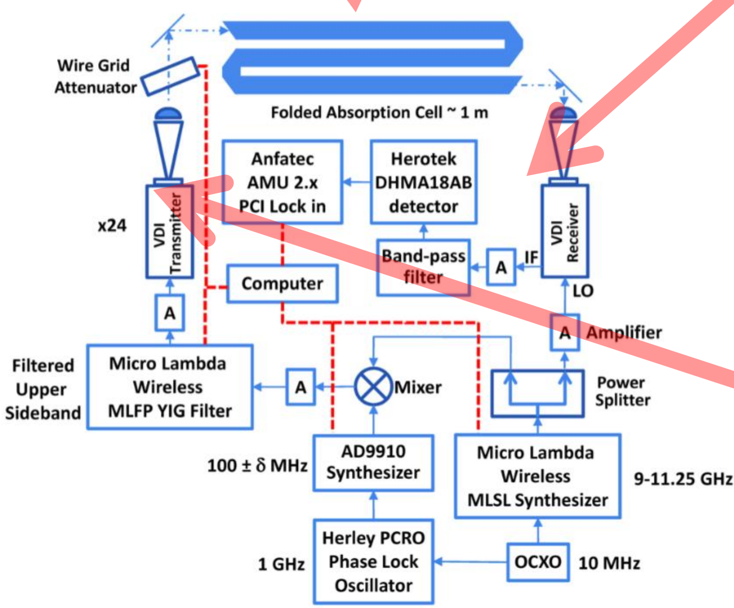
Broad Line of Chip Level IC Through 100 GHz Commercially Available in Large Quantity



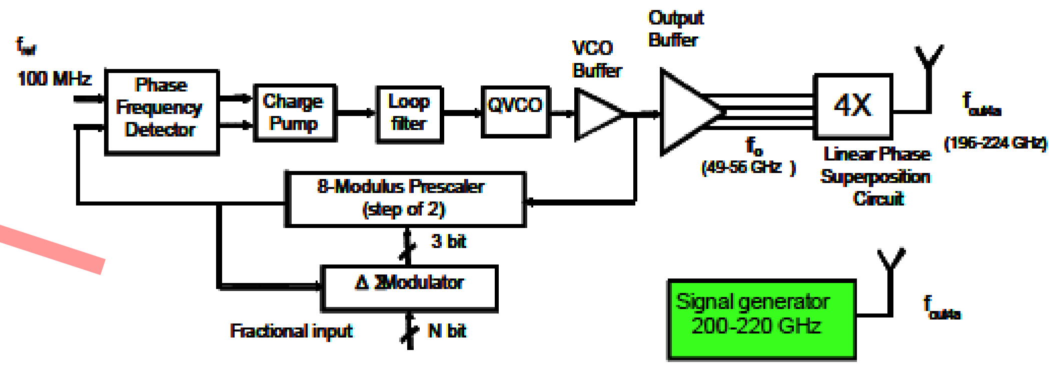
CMOS Integration for 240 GHz*

Antennas: Rashaunda Henderson (UT-D)





Receiver: Bhaskar Banerjee (UT-D)



Transmitter: Kenneth O (UT-D)

*Sponsored by the Semiconductor Research Corporation

Summary: Submillimeter Sensors of Static Samples

- **Dominates a significant portion of spectroscopic sensor space**
  - Absolute specificity
  - Extremely small samples with good sensitivity
  - Low atmospheric clutter limits (1 ppt)
  - Favorable trades of sensitivity for speed (agility of electronic synthesis)
- **Clear path to small and inexpensive implementations**
  - Wireless technology and CMOS
  - Electronic synthesis provides size independent resolution
  - Small sample requirements allow less elaborate vacuum systems
- **Challenges and opportunities**
  - Limits on applicability to larger molecules – unclear bounds – not as general as MS or GC
  - Vacuum requirements
    - Significant up side potential – fundamental limits very favorable – infant development

Consequences of the Physics

Optimum pressure is ~ 10^{-5} atmospheres (Doppler) and sample is static

=> very small sample requirements
=> small sampling volumes for large preconcentration gains (1 liter STP - 10^5 gain)
=> vacuum requirement greater than in IR/Op
=> atmospheric clutter limit ~1 ppt (aided by spectroscopic specifics as well)

Electronic sources are

=> essentially delta functions, even in Doppler limit
=> frequency agility to optimize photon use

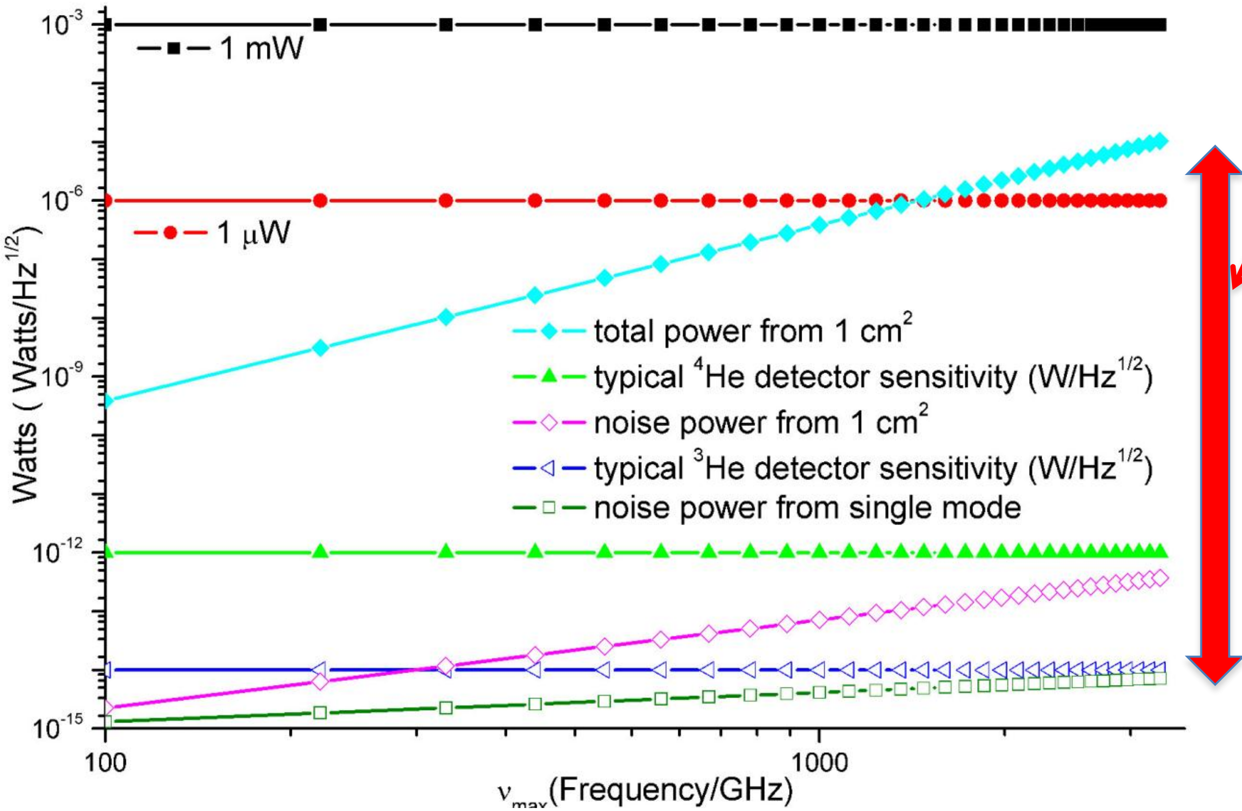
Small Power provides very high brightness

=> path to very small and inexpensive technology

Spectral density strong function of molecular size

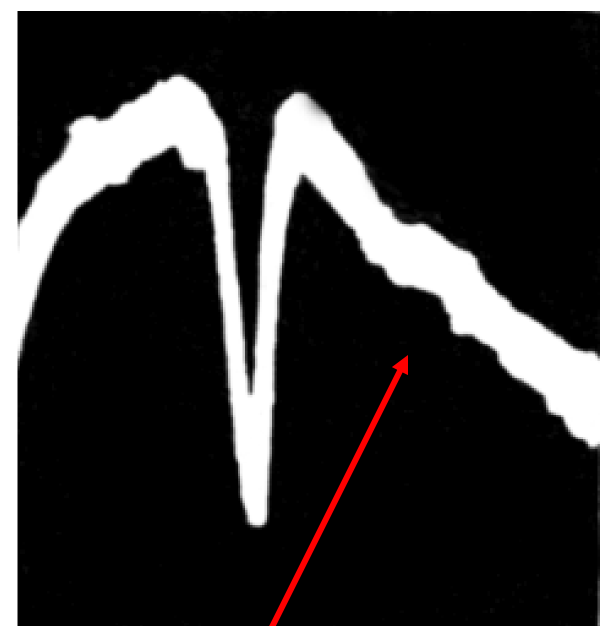
=> large molecule limit with static ambient samples

The THz is *VERY* Quiet even for CW Systems in Harsh Environments



10^{10} Misconception

Experiment: SiO *vapor* at ~1700 K



All noise from 1.6 K detector systemm

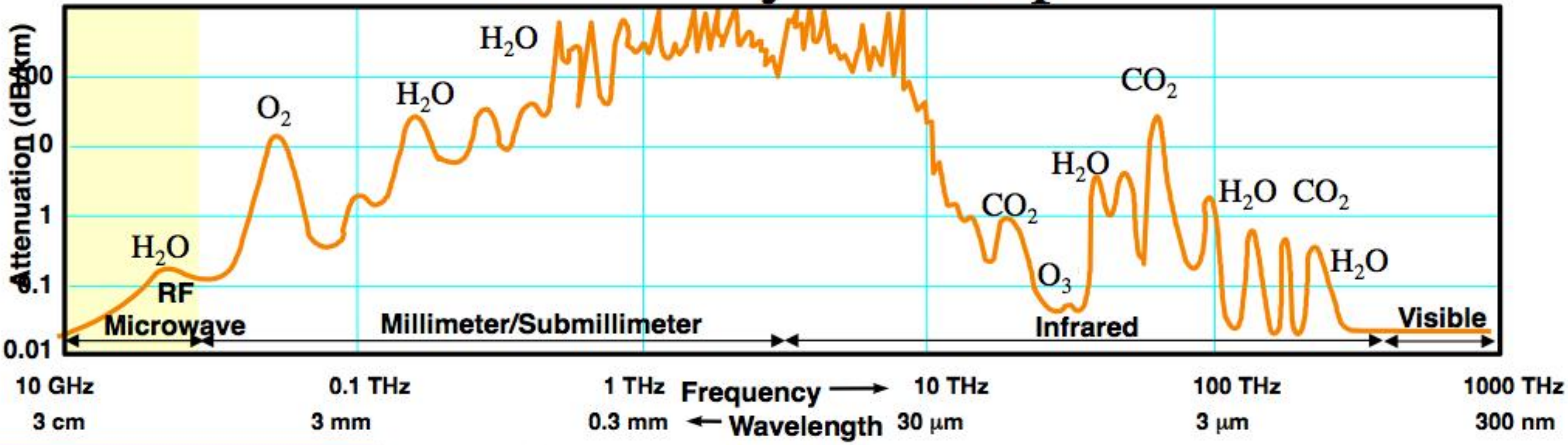
Noise, detectors, and submillimeter–terahertz system performance in nonambient environments

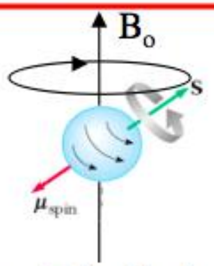
Frank C. De Lucia

Department of Physics, Ohio State University, Columbus, Ohio 43210

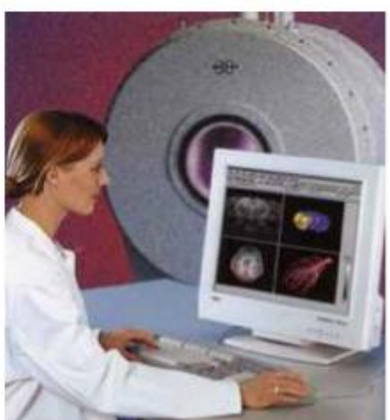
Received June 23, 2003; revised manuscript received February 10, 2004; accepted March 10, 2004

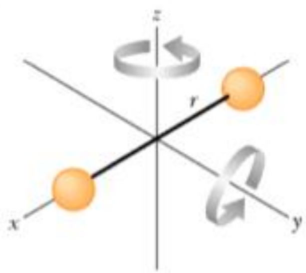
THz Analytical Gap





Bruker BioSpin MRI





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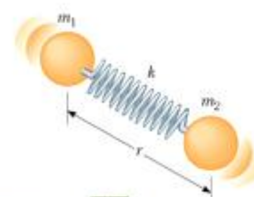
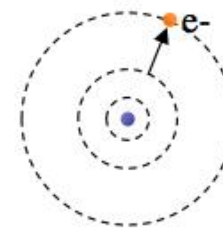


Bruker FTIR's

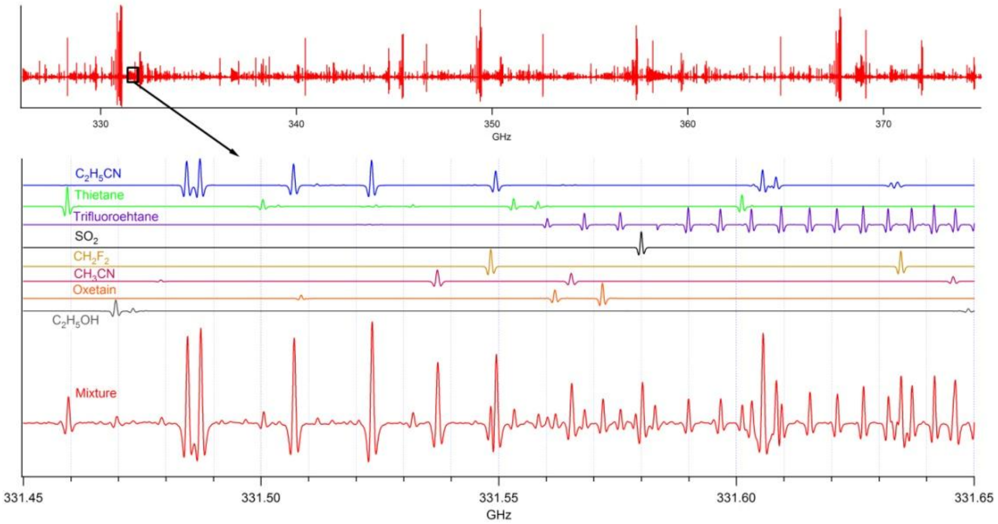


International Light

Sub-Millimeter Wave Introduction

•High resolution SMM spectroscopy exploits rotational transitions of molecules
•100 000 resolution elements and complex thermally excited signature provides 'absolute' specificity

300 K Static Equilibrium Sample



Technique ideal for gas phase detection

- High specificity
- High sensitivity
- Low false alarm rate
- Fast measurement and analysis
- Broad range of analytes
- Small, low power technology

Rapid technology commercialization in the MM/SMM makes this long held promise a practical foundation for a entirely new sensor approach

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

$$P_n' \approx \sqrt{kT\Delta\nu P_c} = \sqrt{(5\times10^{-14})(10^{-3})} \approx 10^{-8}W$$

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

Sensitivity Comparisons[1,2]

- For variety of Op/IR experiments

- Similar in terms of ppx sensitivity with wide variation according to
- Choice of molecule
- Technical implementations
- Generality
- Specificity

- Because the optimum pressure is proportional to Doppler width

- 100 – 1000 less sample smaller sample in the SMM
- ~10^{-14} moles for HCN, ~ 5 x 10^{-14} moles for CH_3CN, and 10^{-12} moles for $C_2H_4Cl_2$

- For radicals (strong electronic transitions) detection limits in the ppt range have been reported.

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1. Without sorbant collector
2. "Submillimeter spectroscopy for chemical analysis with absolute specificity," Ivan R. Medvedev, Christopher F. Neese, Grant M. Plummer, and Frank C. De Lucia, Opt. Lett. 35, 1533 (2010).