Terahertz Spectroscopy Short Course

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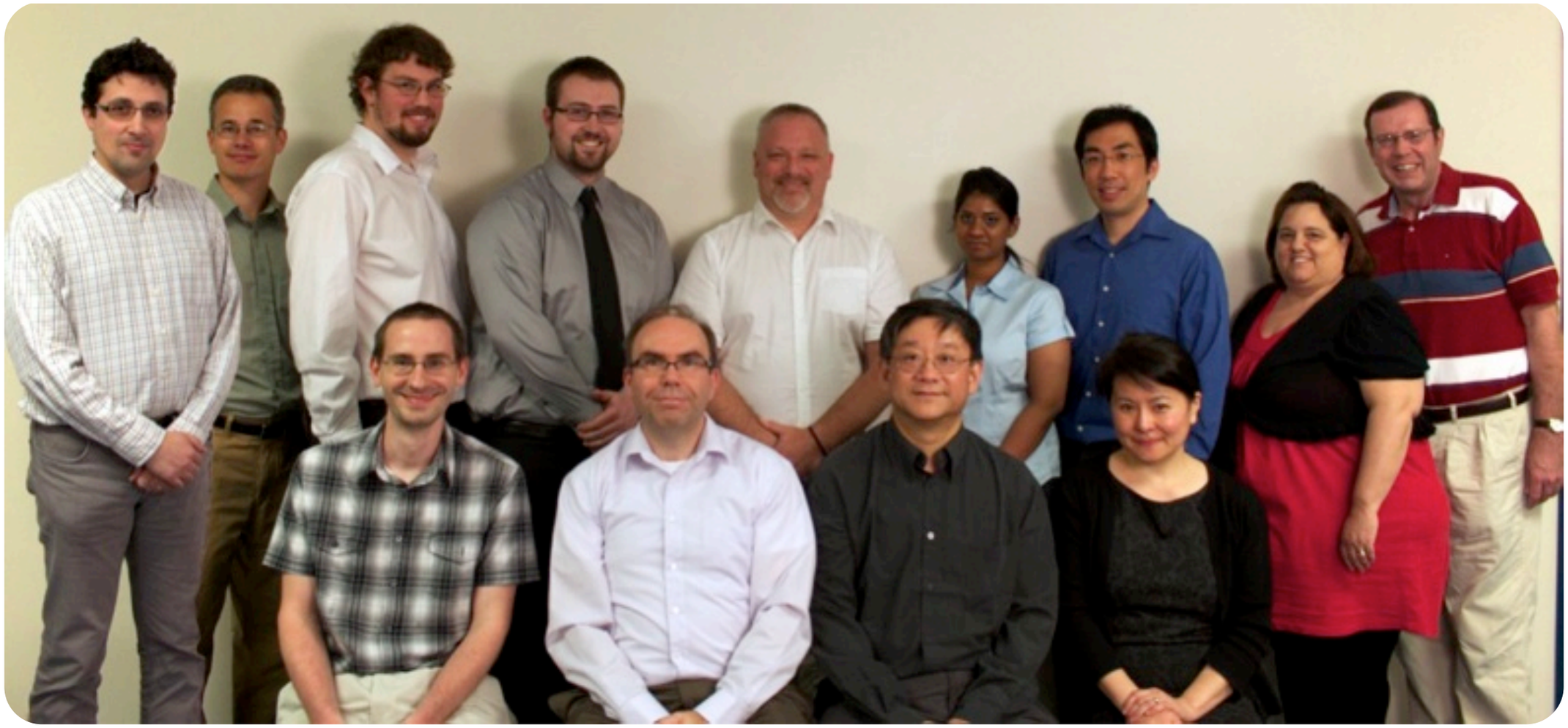
Scope of the Course

- Company overview
- Terahertz time-domain systems
- Measurement procedure
- Application examples
- Instrumentation overview

Zomega Terahertz Corporation

Who We Are



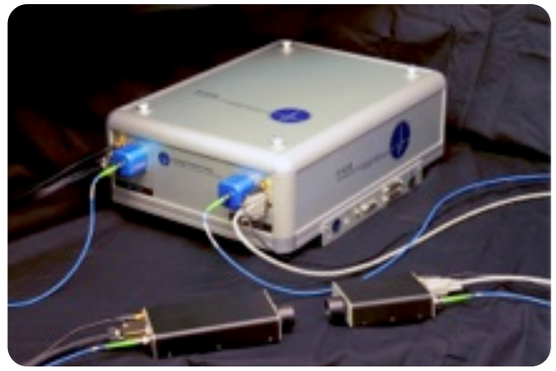
- Founded in 2005 to design, fabricate, and commercialize Terahertz systems and applications
- Core technology covered by seven patents issued and pending
- Only company that offers high data-rate, portable and handheld Terahertz systems
- Worldwide sales and service
- 40+ years of combined experience in Terahertz research and development

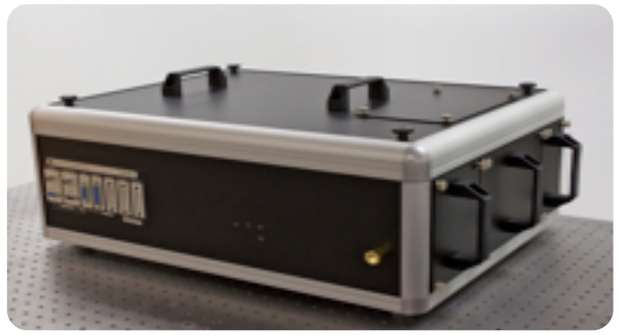
Portfolio

Systems

Mini-Z, Micro-Z, FICO, ZAP, Z3 series

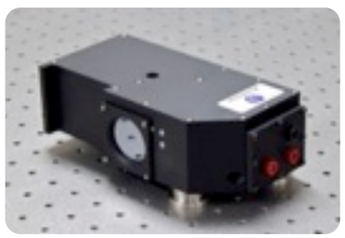






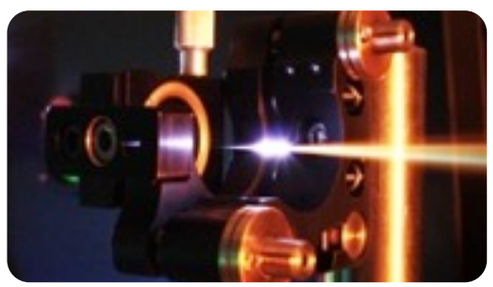
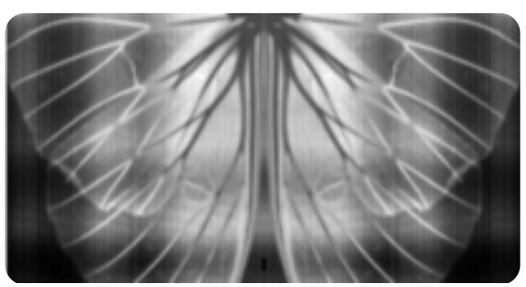
Components

Auto-balanced detector, high-voltage modulators, Photo-conductive antennas, ZAP detector...

Research

Spectroscopy, Non-destructive evaluation, Imaging, Plasma systems

Product Development Expertise

2007::Mini-Z

- ✓ First portable and completely integrated THz spectrometer
- ✓ Real-time data
- ✓ Reflection and transmission geometry
- ✓ Turnkey operation
- ✓ Open architecture
- ✓ Integrated design

2011::Micro-Z

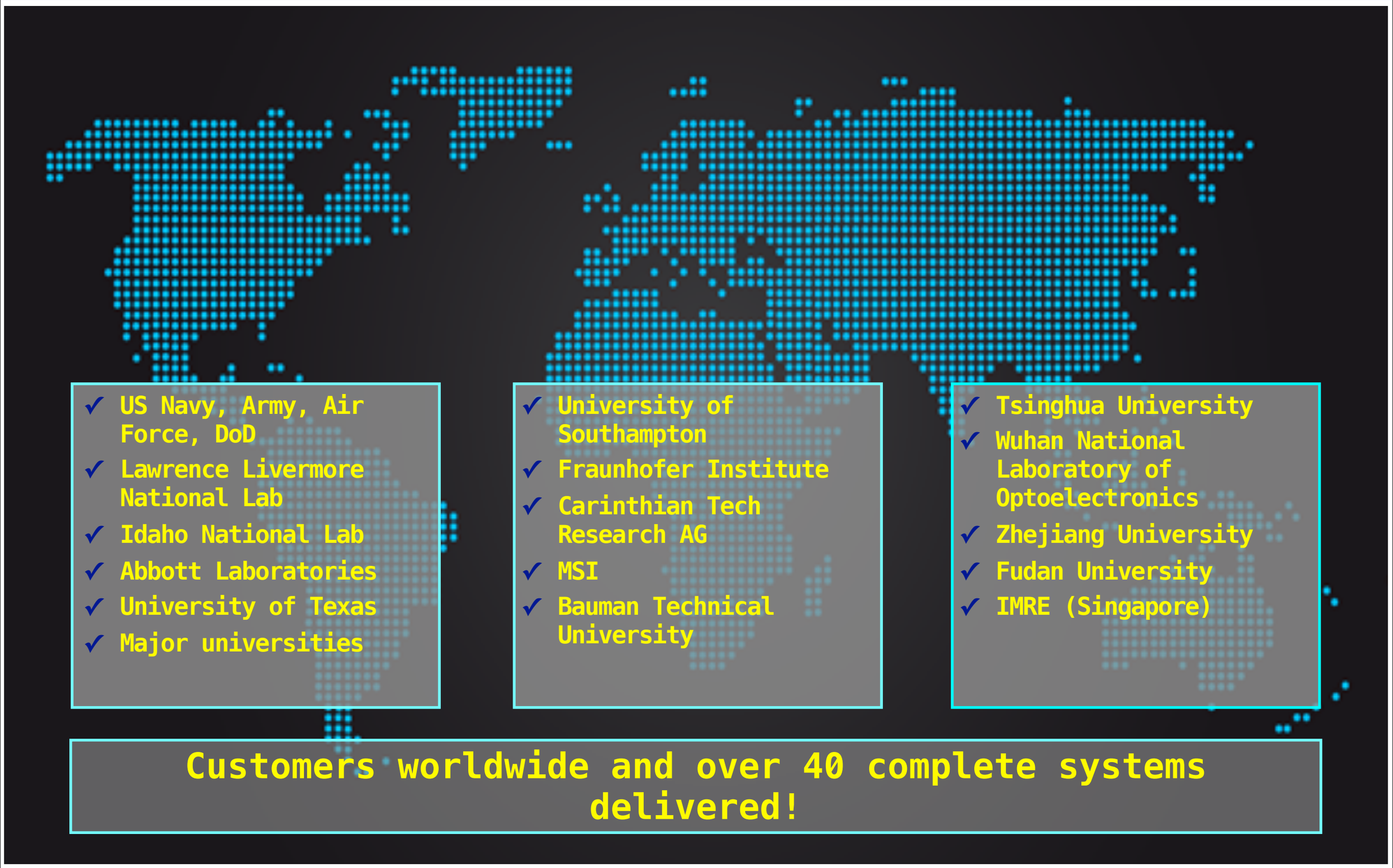
- ✓ First handheld and battery operated THz spectrometer
- ✓ Real-time data
- ✓ Standoff reflection measurement
- ✓ Specific chemical signature identification
- ✓ Integrated scattering baseline correction
- ✓ User expandable library

	2004	2008	2012
Size / Weight	Bench-size / >100 lbs.	Portable / ~15 lbs.	Handheld, battery operated / ~5 lbs.
Data Rate	Tens of minutes per waveform	~10 Hz	~500 Hz
SNR	~50 dB	~60 dB	~70 dB
Ease of Use	Low, specialized staff	Medium, technician level	High, non-expert user
Environment	Laboratory only	Office, workbench	Open field

Differentiation

- Compact form factor systems
  - ✓ Portable and handheld
  - ✓ User-friendly
- High data rate
  - ✓ Waveform rates between 500 Hz to 2 kHz
  - ✓ High number of inspection per minute (real-time and in-line inspection)
- Open software architecture
  - ✓ Integration with external systems and custom application development
- Only company commercializing systems based on Electro-Optic (EO) sampling as detection
  - ✓ EO sampling is more robust, broader bandwidth, and higher SNR than using photo-conductive antennas

Customers



- ✓ US Navy, Army, Air Force, DoD
- ✓ Lawrence Livermore National Lab
- ✓ Idaho National Lab
- ✓ Abbott Laboratories
- ✓ University of Texas
- ✓ Major universities

- ✓ University of Southampton
- ✓ Fraunhofer Institute
- ✓ Carinthian Tech Research AG
- ✓ MSI
- ✓ Bauman Technical University

- ✓ Tsinghua University
- ✓ Wuhan National Laboratory of Optoelectronics
- ✓ Zhejiang University
- ✓ Fudan University
- ✓ IMRE (Singapore)

Customers worldwide and over 40 complete systems delivered!

Partners and Distributors

Partners

TOPTICA PHOTONICS
A Passion for Precision.

Distributors

soliton

OPTOPRIM

INDECO,INC.
Independence & Collaboration

TERASPECTR
ТЕРАГЕРЦОВАЯ СПЕКТРОСКОПИЯ

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Titan Electro-Optics Co.,Ltd.

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Time-domain Systems

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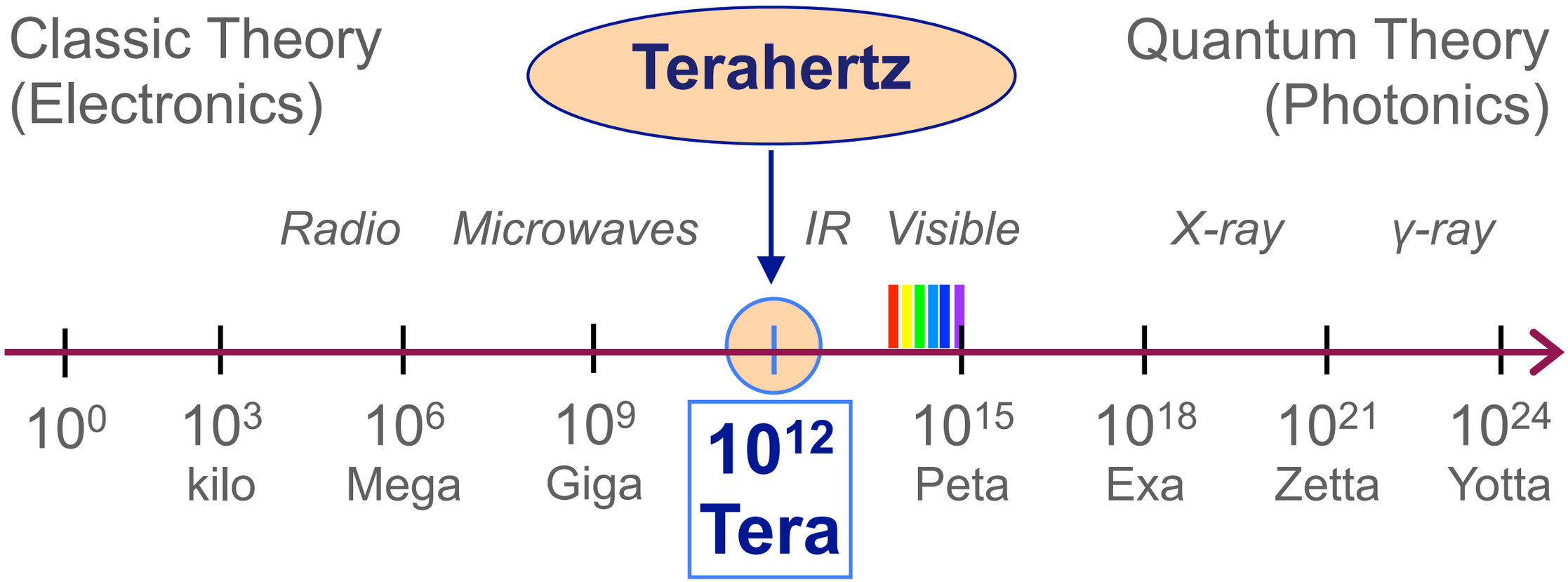
The Terahertz Frequency Band



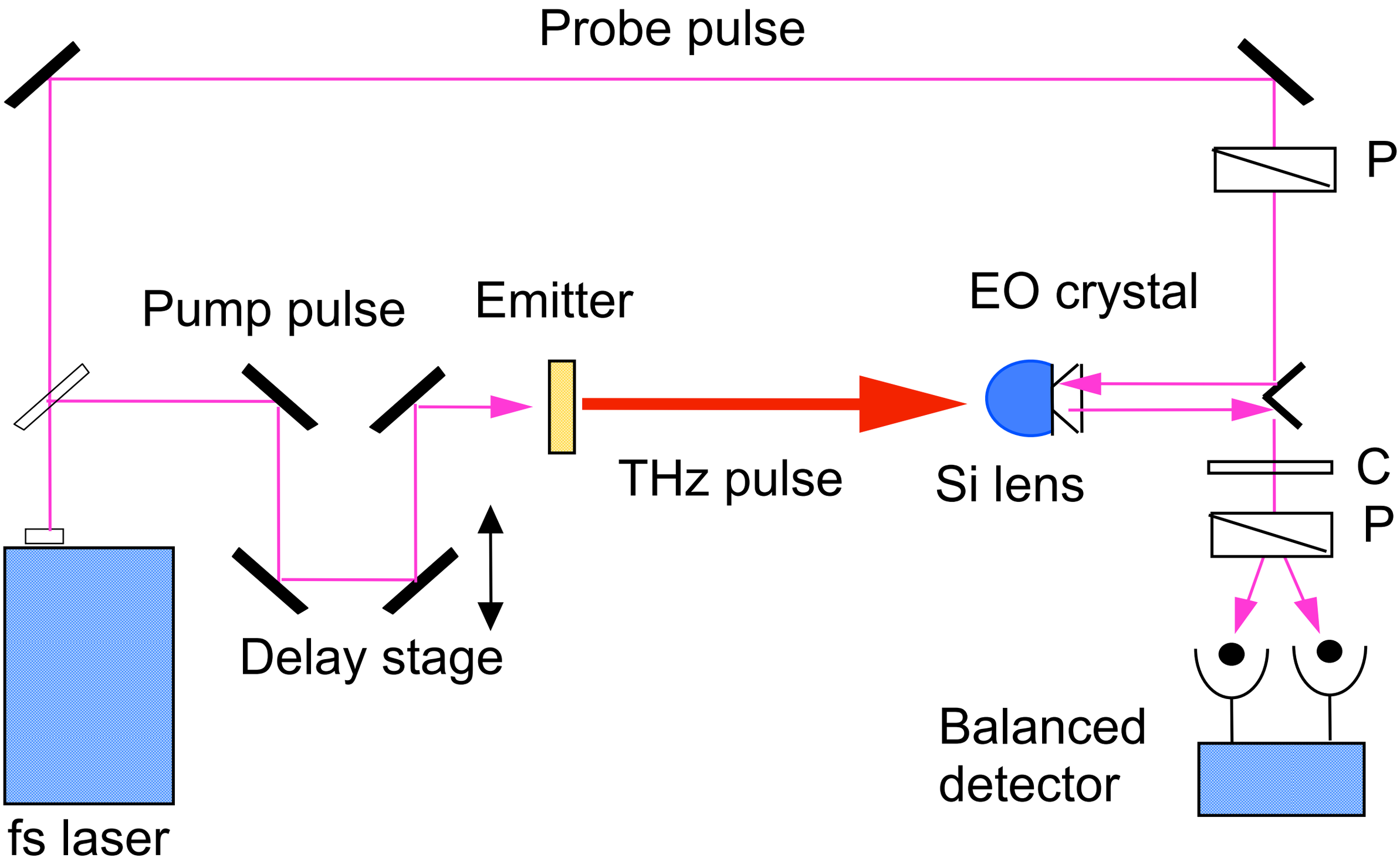
Frequency (Hz)

1 THz ~ 33 cm^{-1} ~ 1 ps ~ 300 um ~ 4 meV ~ 47 K

Terahertz Features

- **See-through:** penetrates most materials
- **Pinpoint measurement and imaging:** excellent spatial resolution (sub-mm)
- **Molecular fingerprint:** spectroscopic identification
- **Safety:** non-ionizing radiation
- **Non-contact:** standoff emission/detection

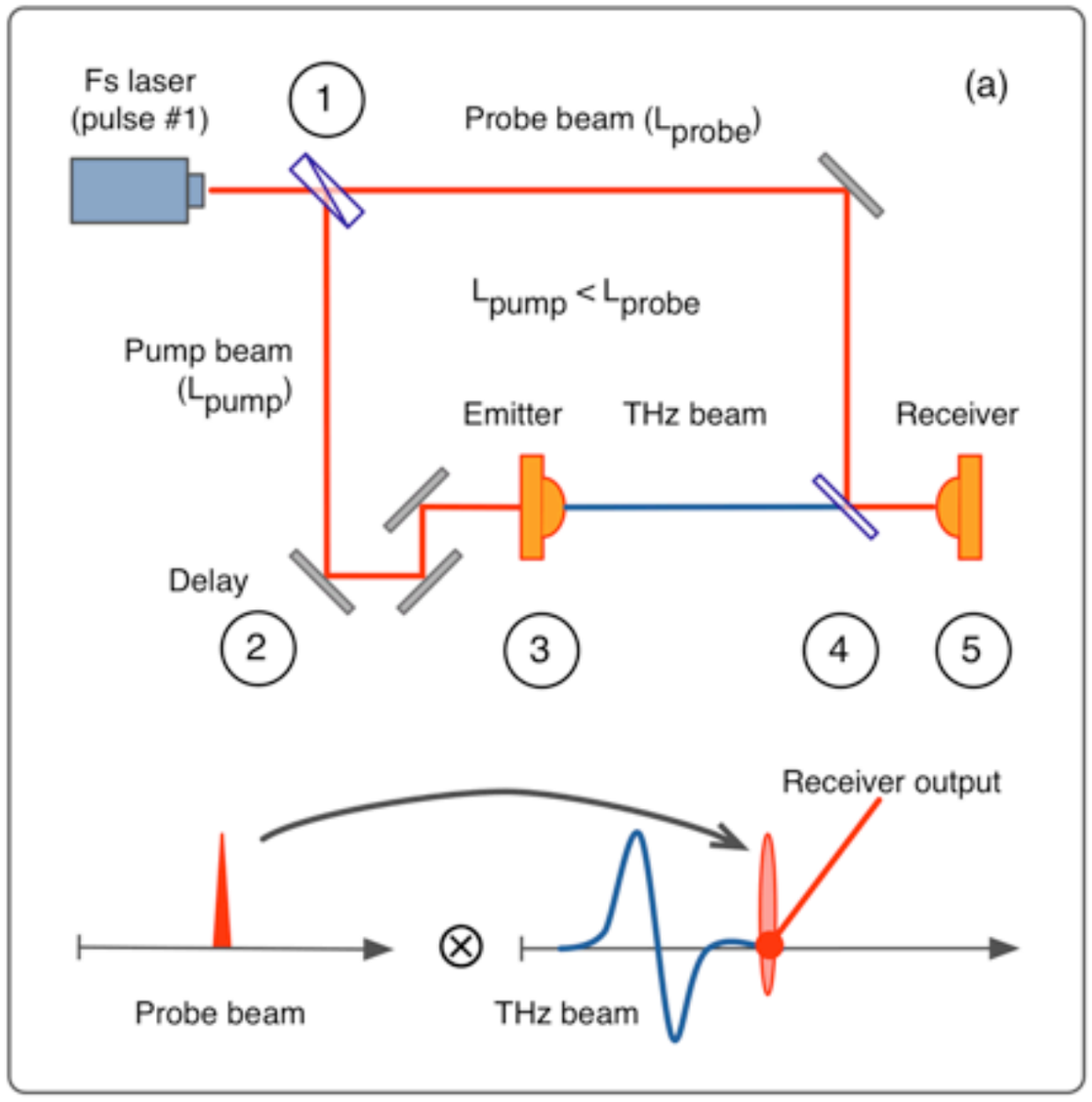
Terahertz Time Domain System

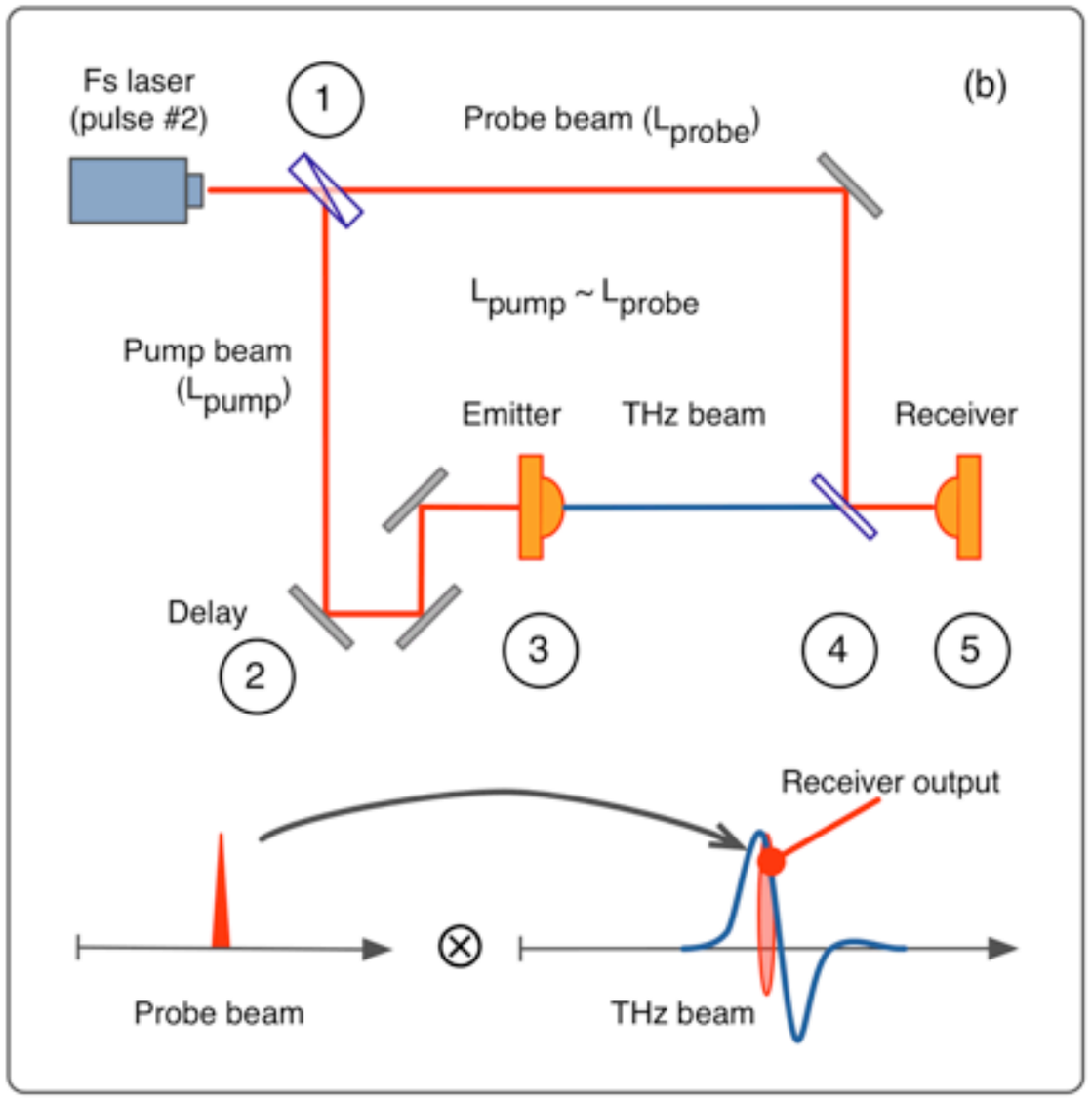


Pump-probe Process

- Splitting
  - ✓ The source fs laser pulse is separated into pump and probe
- Delay
  - ✓ Changes the relative path (time difference) between pump and probe
- Transient generation
  - ✓ Pump generates the THz pulse
- Probe-transient (THz) merging
  - ✓ Probe is like a delta function compared with the THz pulse
  - ✓ The response of the detector is proportional to the convolution of the probe beam and THz pulse
- Change delay and repeat
  - ✓ Change the time delay for the next laser pulse, the probe samples another point of the THz pulse generated by the pump

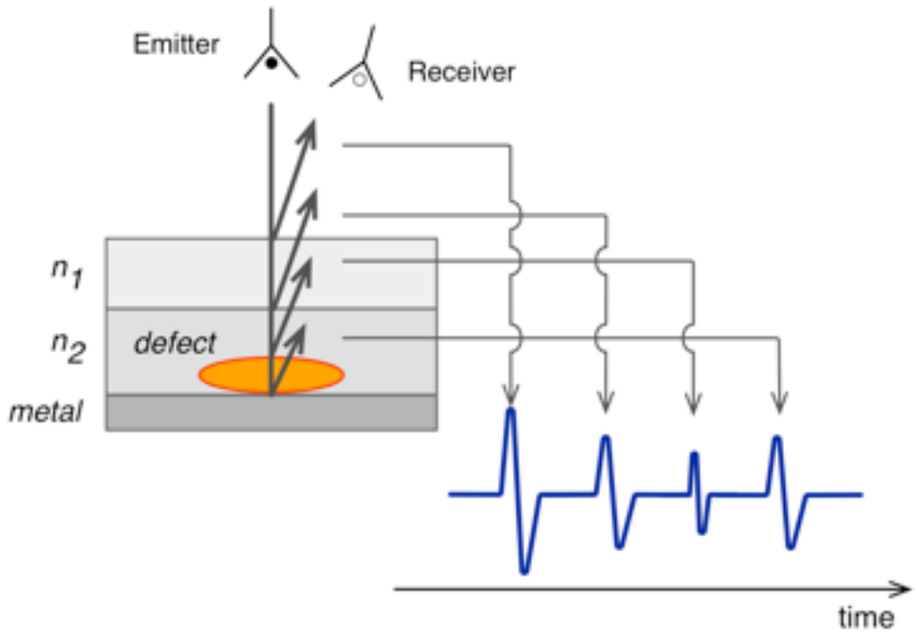
Pump-probe Process (cont.)



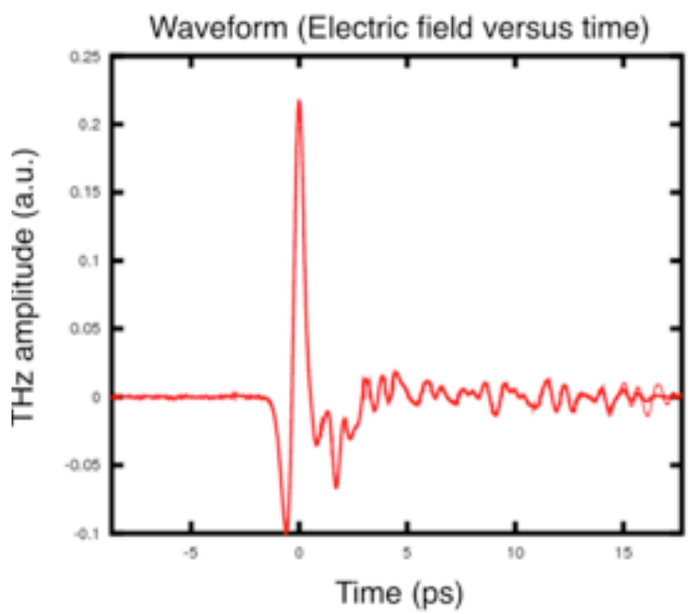


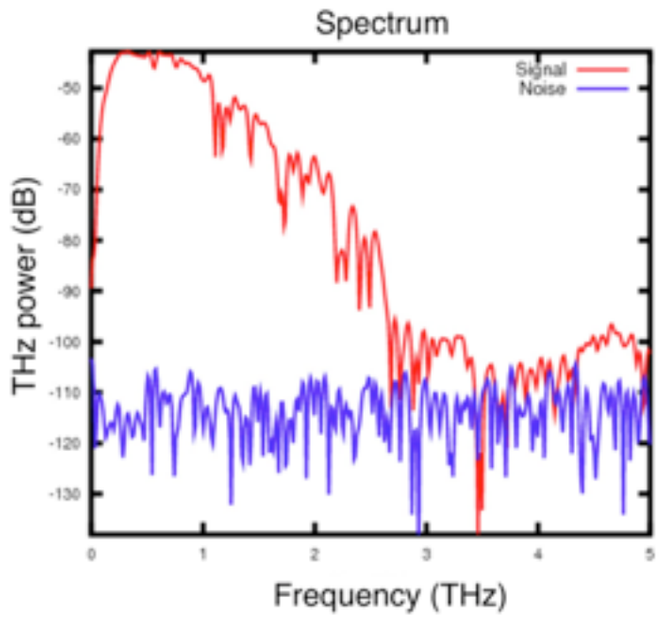
Operation Modes

Time-domain



Frequency-domain





- **Non-destructive evaluation**
  - ✓ Cracks, voids, and other structural defects
  - ✓ Thickness and coatings measurement
  - ✓ Corrosion inspection

- **Spectroscopy**
  - ✓ Pharmaceutical characterization and drug discovery
  - ✓ Chemical and biological threat assessment
  - ✓ Explosive detection

Spectroscopic Measurement

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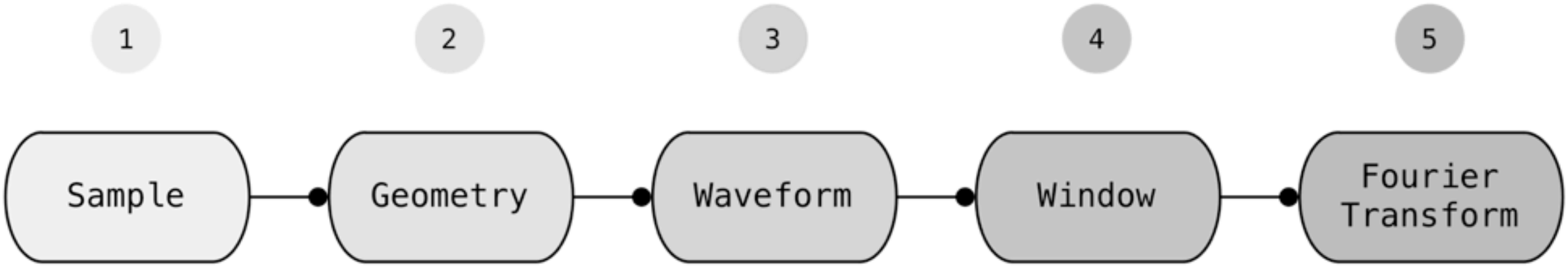
Spectroscopy: Measurement Flow



> Form > Scattering > Absorbance > Index of refraction	> Transmission > Reflection	> Reference > Sample > Noise > Averaging > Rate	> Shape > Length	> Magnitude > Phase > SNR

Sample Characteristics

- Form
  - ✓ Liquid, solid, gas → Frequency Resolution
- Scattering
  - ✓ Particle size, homogeneity → Bandwidth
- Chemical composition
  - ✓ Resonances, spectral fingerprints → Absorbance, SNR
- “Optical” properties
  - ✓ Complex index of refraction → Delay, Fresnel losses

Scattering

- Change of direction of photons (λ) due to the finite size of particles (d)

- d << λ –> Rayleigh scattering $\sigma \approx \frac{d^6}{\lambda^4}$
  - ✓ Strongly depends on λ
  - ✓ Affects short wavelengths (high frequencies)

- d >~ λ/10 –> Mie scattering
  - ✓ Depends on particular shape of particle
  - ✓ Need to solve Maxwell's equations
  - ✓ Often, solutions are less λ dependent than Rayleigh
  - ✓ Solutions may show resonances

Absorbance and Optical Constants

- Reference and sample Fourier Transforms

$$\frac{\tilde{F}_s(\omega)}{\tilde{F}_r(\omega)} = A(\omega)e^{-j\phi(\omega)}$$

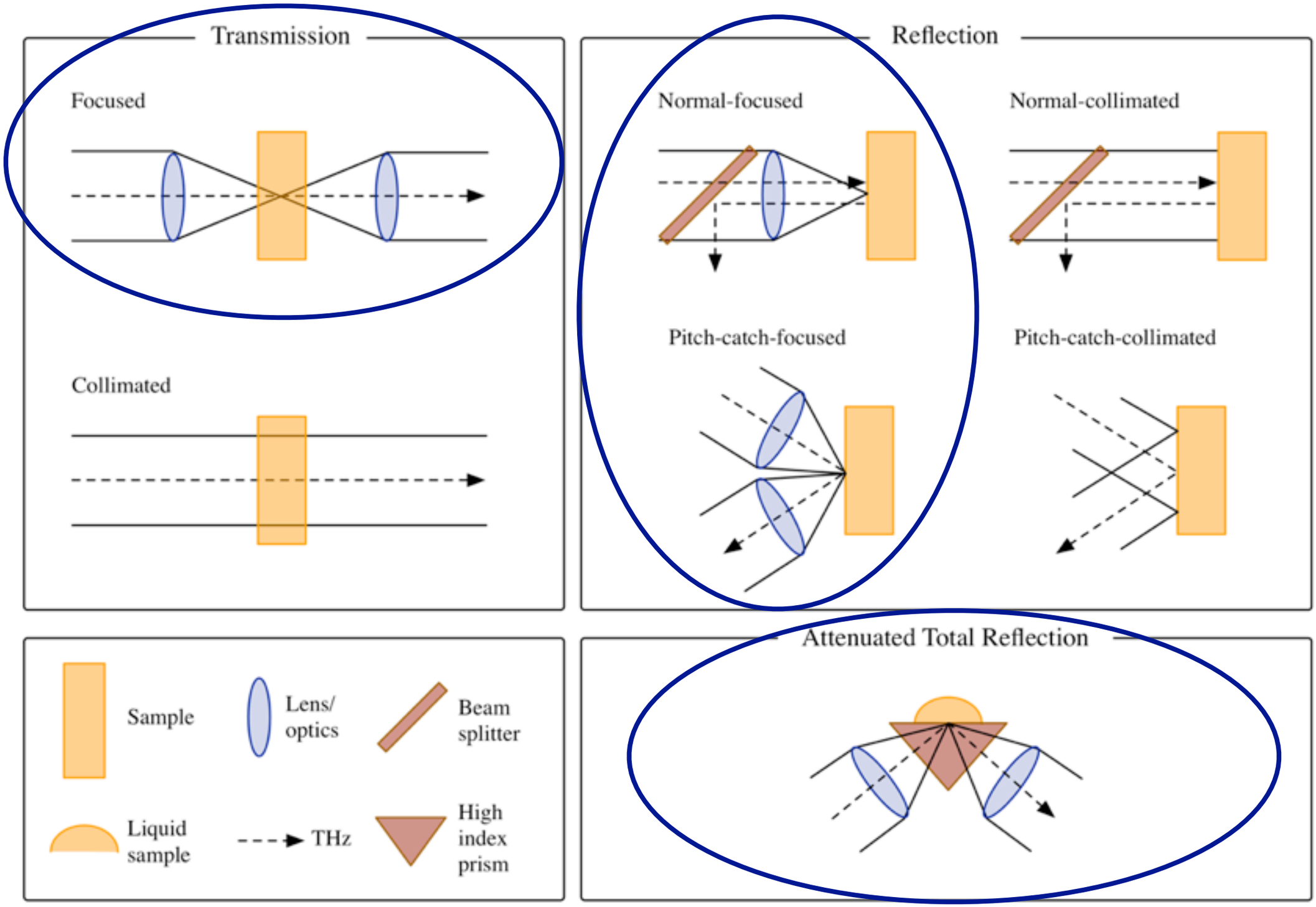
- Complex index of refraction $\tilde{n}(\omega) = n(\omega) - jk(\omega)$
- Parameters calculation

$$n_s = 1 + \phi(\omega)\frac{c_0}{\omega d} \qquad k_s = \frac{c_0}{\omega d} ln\left(\frac{4n_s(\omega)}{A(\omega)\left(n_s(\omega)+1\right)^2}\right) \qquad \alpha(\omega) = \frac{2\omega}{c_0}k_s$$

Sampling Window

- Sampling window affects frequency resolution and sensitivity
- Wide windows offers high resolution $\Delta\nu = \frac{1}{T}$
- Shape affects leakage
  - ✓ High resolution windows
  - ✓ High dynamic range windows
- Product in time-domain = convolution in frequency-domain

Geometries

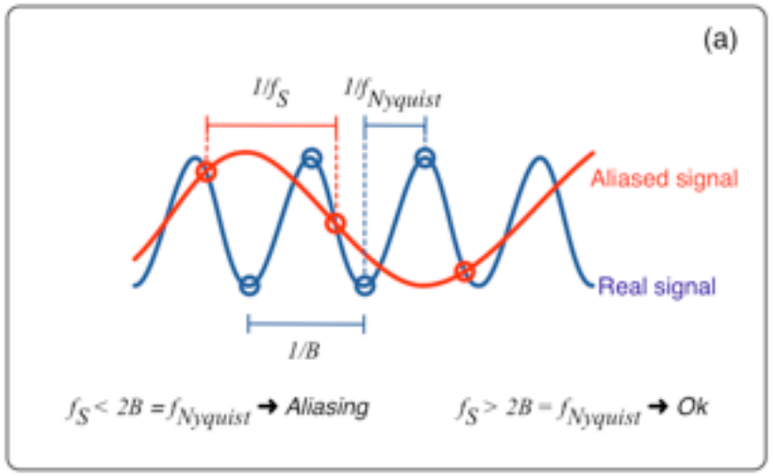

Transmission
Focused
Collimated
Reflection
Normal-focused
Normal-collimated
Pitch-catch-focused
Pitch-catch-collimated
Sample
Lens/
optics
Beam
splitter
Liquid
sample
THz
High
index
prism
Attenuated Total Reflection

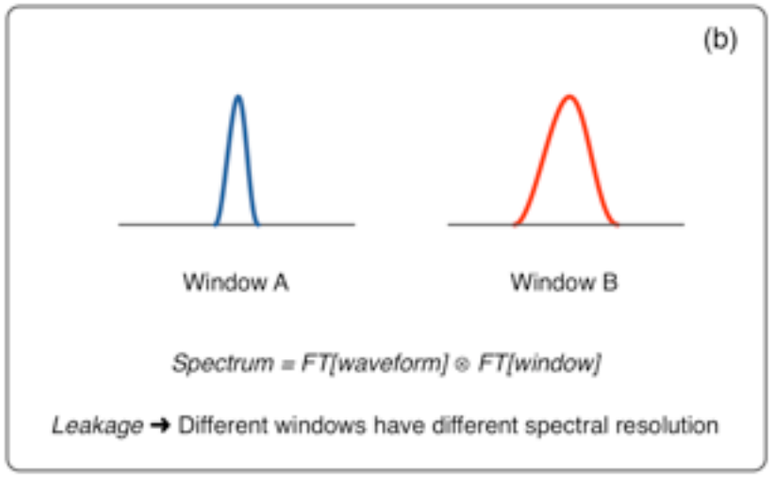
Geometries

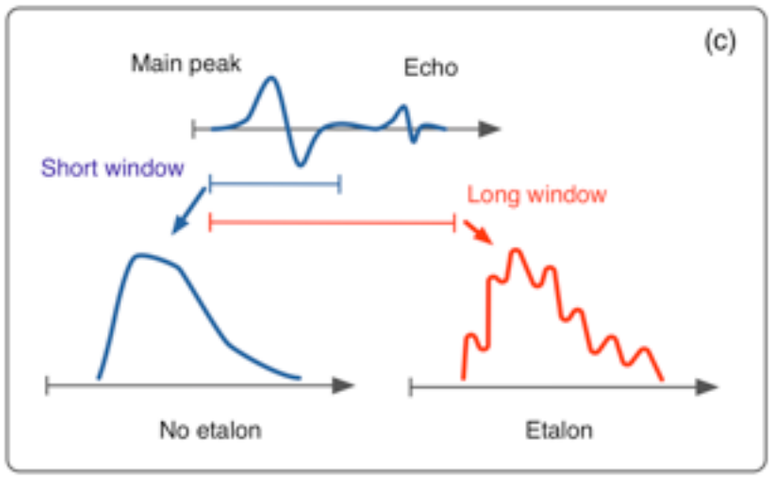
Transmission	Reflection (double-transmission)	ATR
Pros: • Cleaner and easier signal to analyze	Pros: • Larger interaction length • Structural information	Pros: • Very phase sensitive and suitable for liquids
Cons: • Not suited for liquids • Not practical in some cases	Cons: • Lower signal due to loss from beam splitter • Multiple reflections (limited resolution)	Cons: • Must be in contact with sample

Artifacts

- Aliasing
  - ✓ Distortion of the signal resulting from a sampling rate smaller than the Nyquist frequency
  - ✓ High frequencies cannot be recovered
- Leakage
  - ✓ Spreading of energy of a frequency component to neighbor components
- Etalon effect
  - ✓ Echoes from the main peak can generate interference features in the spectrum if they are taken in the same temporal window as the main peak for the Fourier transform



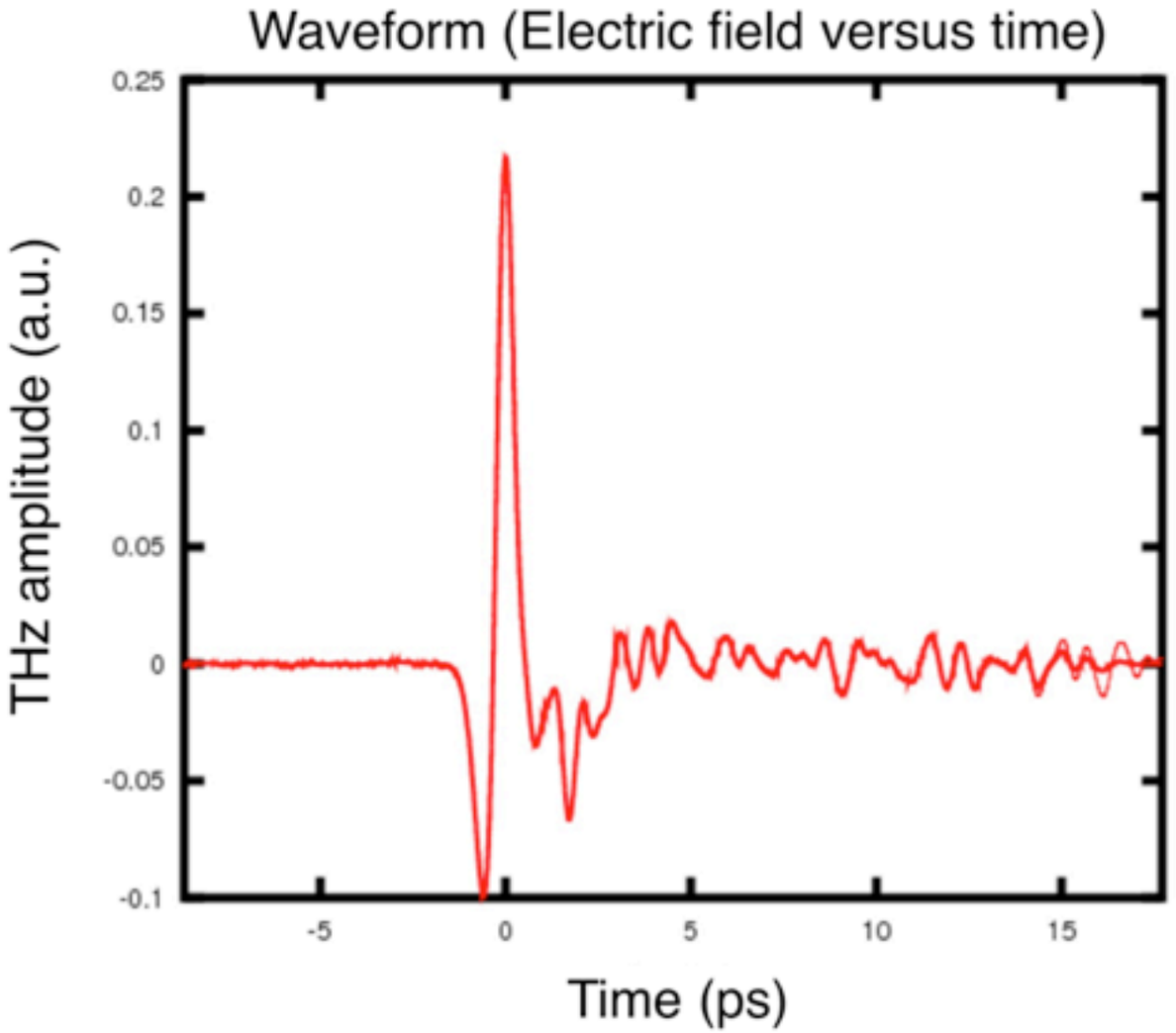


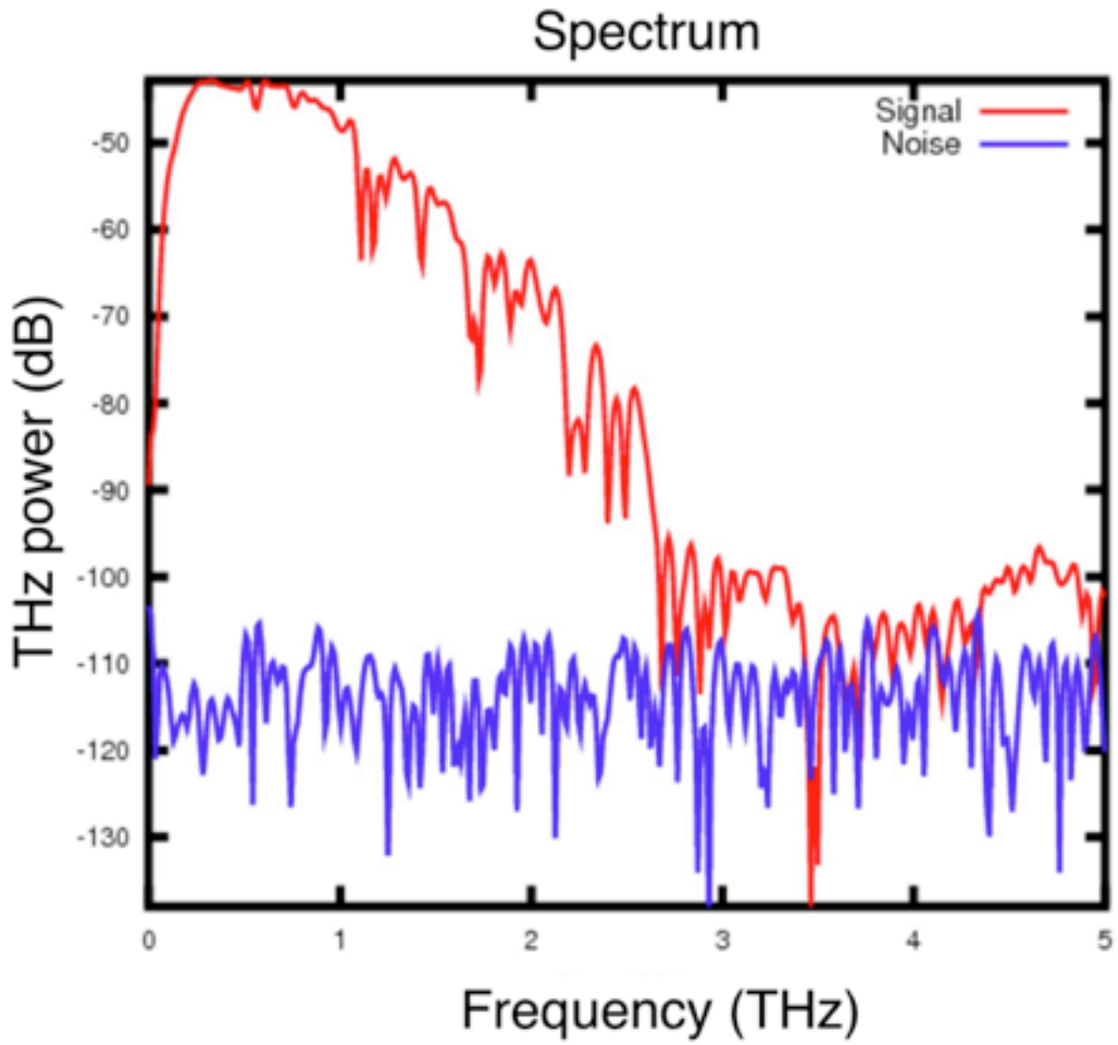


Performance

- Bandwidth
  - ✓ Region in which SNR is greater than a specified threshold
- Frequency resolution
  - ✓ Separation between two frequencies
  - ✓ Related with window length
- Dynamic range
  - ✓ Ratio between the largest and smallest signal without distortion
- SNR
  - ✓ Ratio between signal and noise

Example


Waveform (Electric field versus time)
THz amplitude (a.u.)
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-5
0
5
10
15
Time (ps)


Spectrum
Signal
Noise
THz power (dB)
-50
-60
-70
-80
-90
-100
-110
-120
-130
0
1
2
3
4
5
Frequency (THz)

Best Practices

- Measure a reference before measuring your sample
- Save your data with metadata about what you have measured (label samples)
- Measure and save the noise after you save your data under the same conditions as the signal
- Use consistent time window settings across all samples in an experiment
- Repeat your measurements several times to determine error bars for the measurement
- Repeat your measurements with few different sampling windows
- Be careful with low SNR (<10) regions

Application Examples

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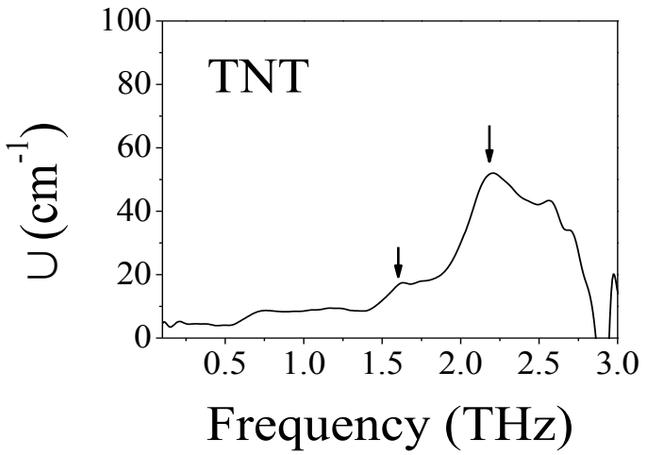
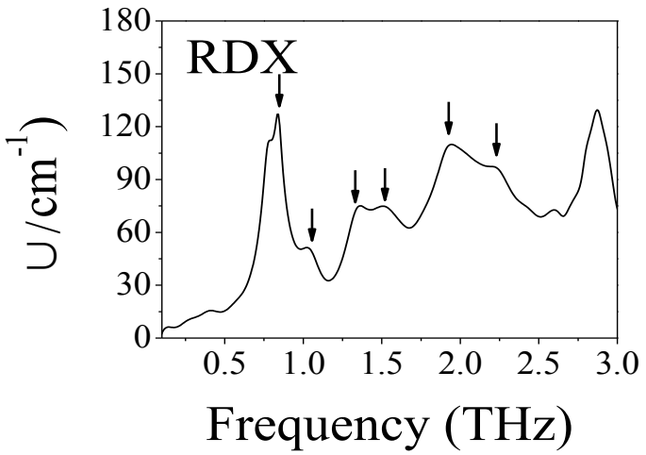
Alternative Techniques

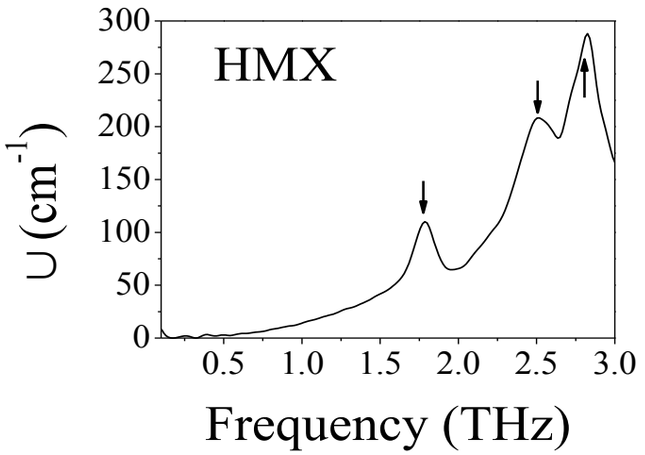
Table 2.2

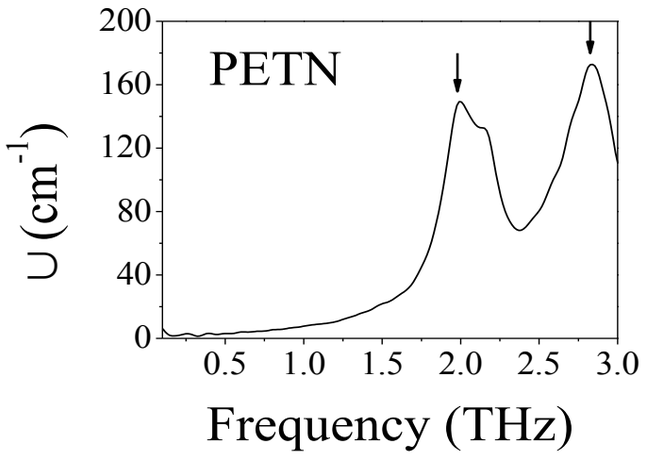
Technique	Strengths	Weaknesses
FTIR	✓ High frequency resolution (~1cm^{-1}) ✓ High sensitivity ✓ Broadband (up to 100 THz)	◉ Cannot interrogate targets under cover ◉ No coherent detection ◉ Need cryogenic conditions for high sensitivity ◉ No real-time data rate
Raman	✓ High frequency resolution (~1cm^{-1}) ✓ Room temperature operation ✓ High sensitivity ✓ High selectivity	◉ Cannot interrogate targets under cover ◉ No coherent detection
TDS	✓ Can interrogate targets under cover ✓ Room temperature operation ✓ Coherent detection (amplitude and phase data) ✓ High selectivity ✓ Real-time data rate	◉ Lower frequency resolution than FTIR (~10cm^{-1}) ◉ Narrower bandwidth than FTIR (up to 5 THz with standard TDS; up to 20 THz with TDS ABCD system)

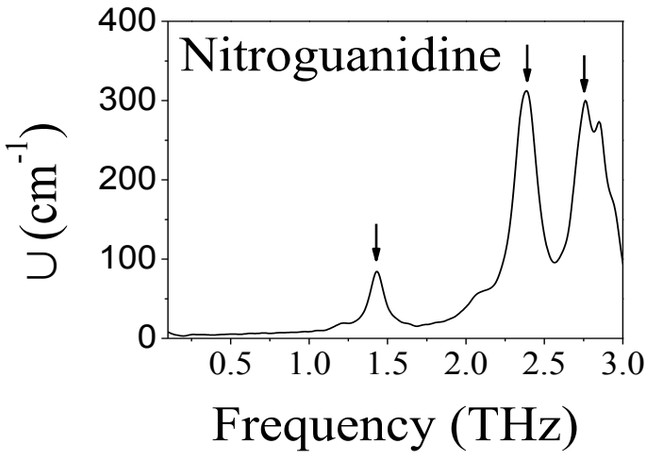
Explosives Identification

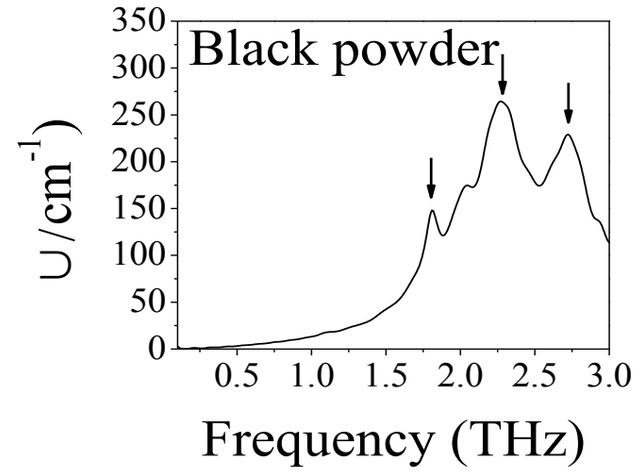


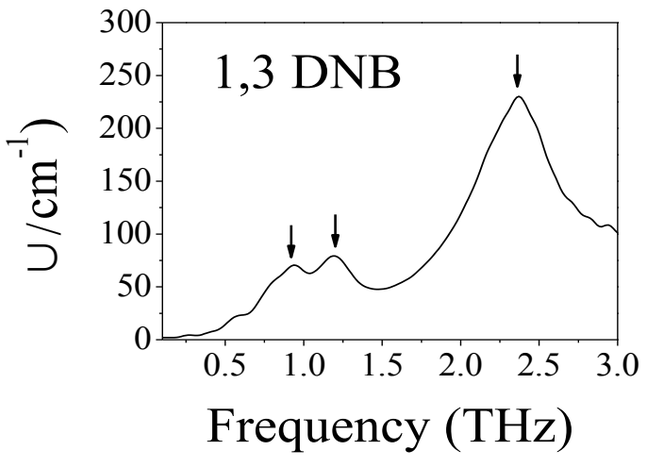


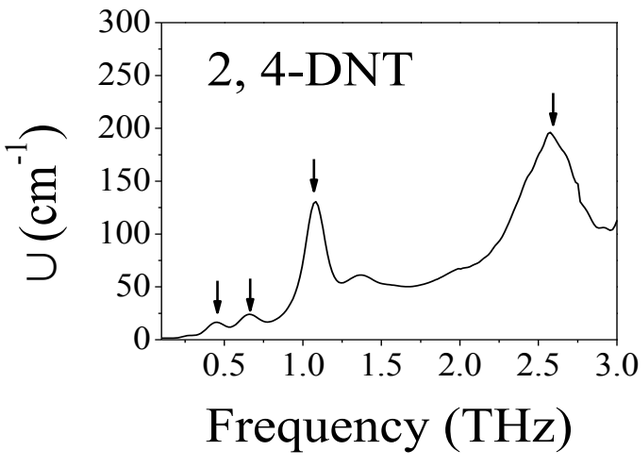


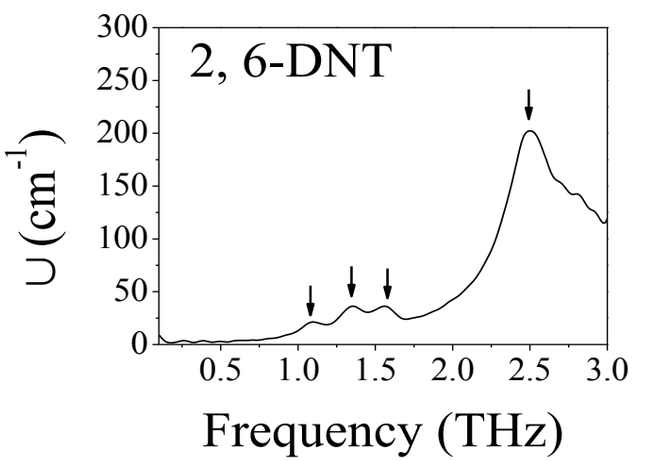




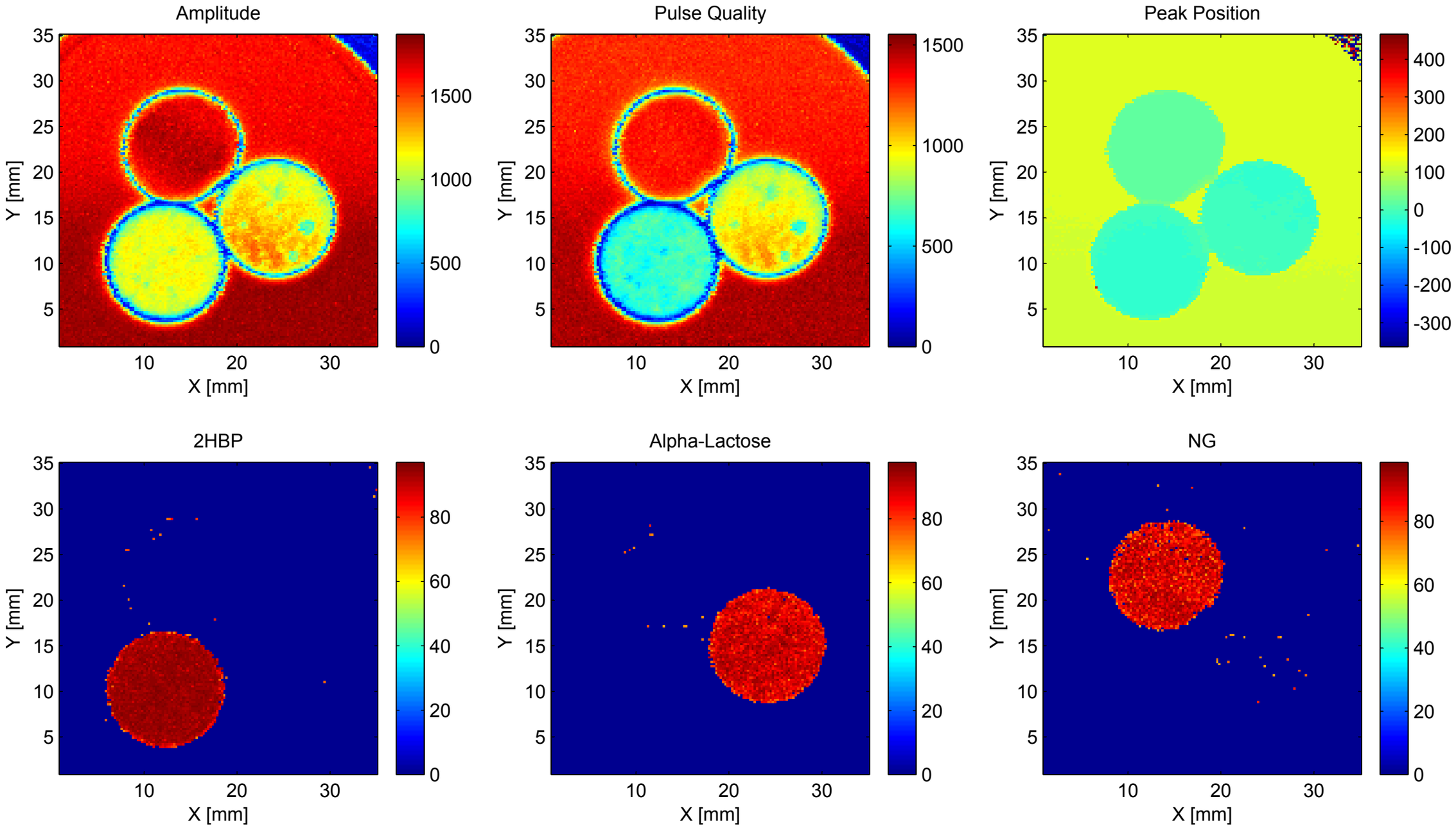




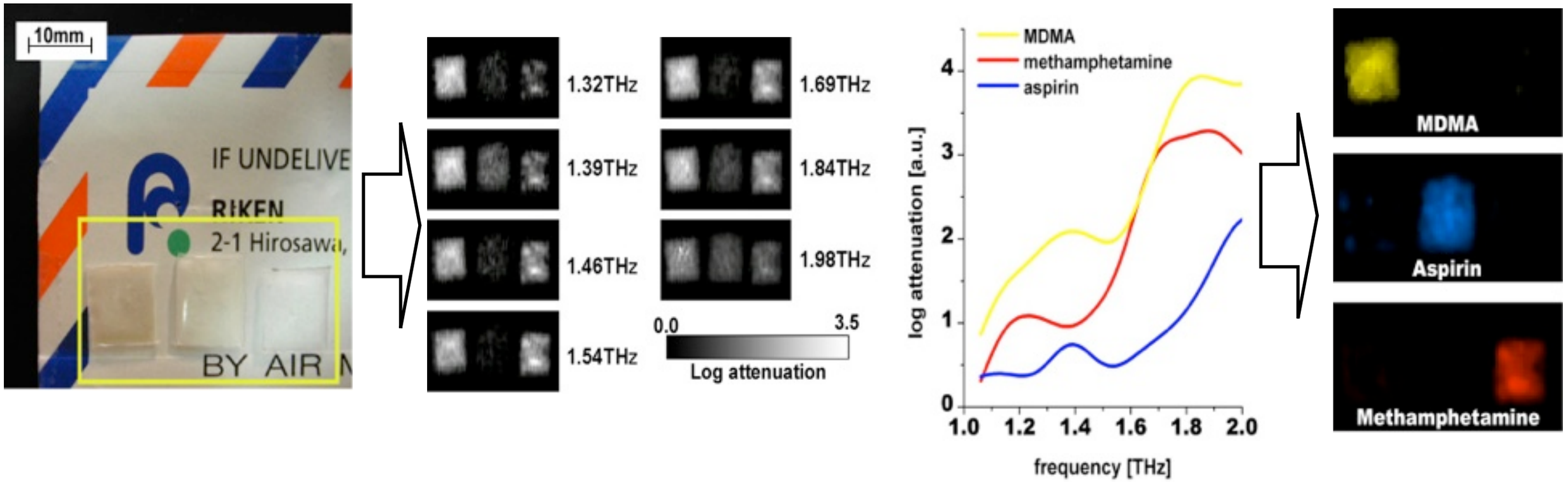




Spectroscopic Imaging

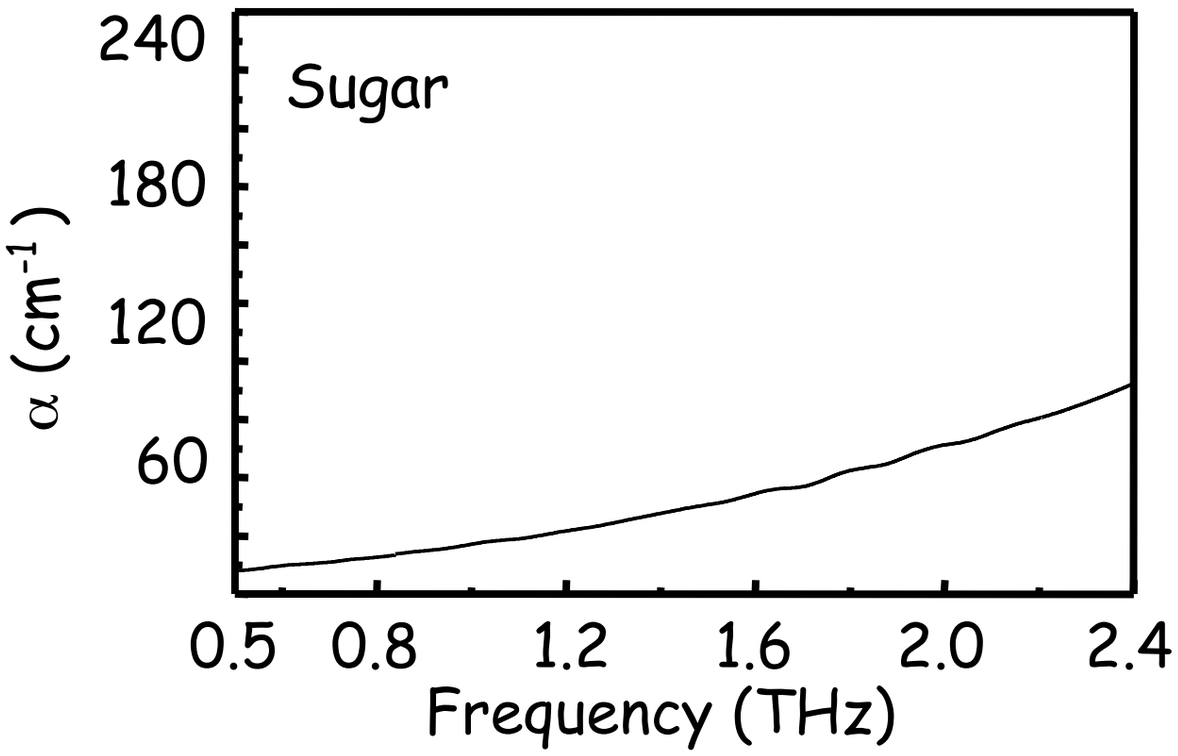


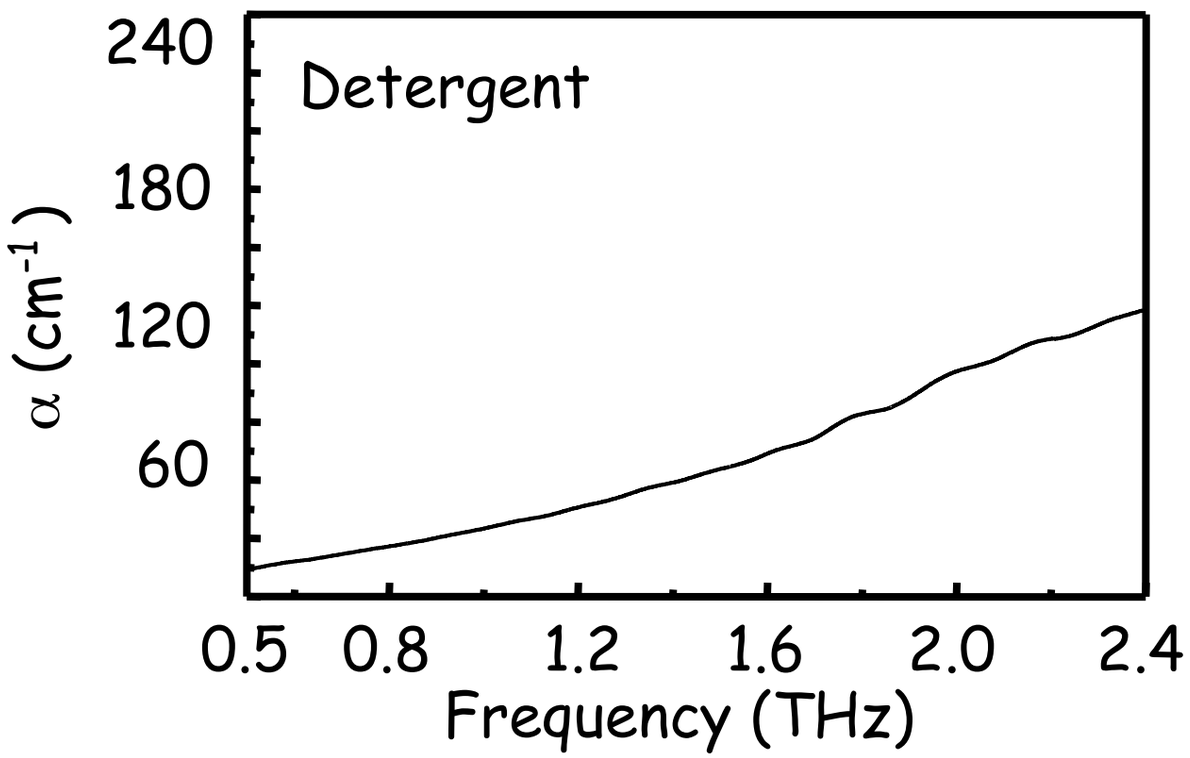
Spectroscopic Imaging

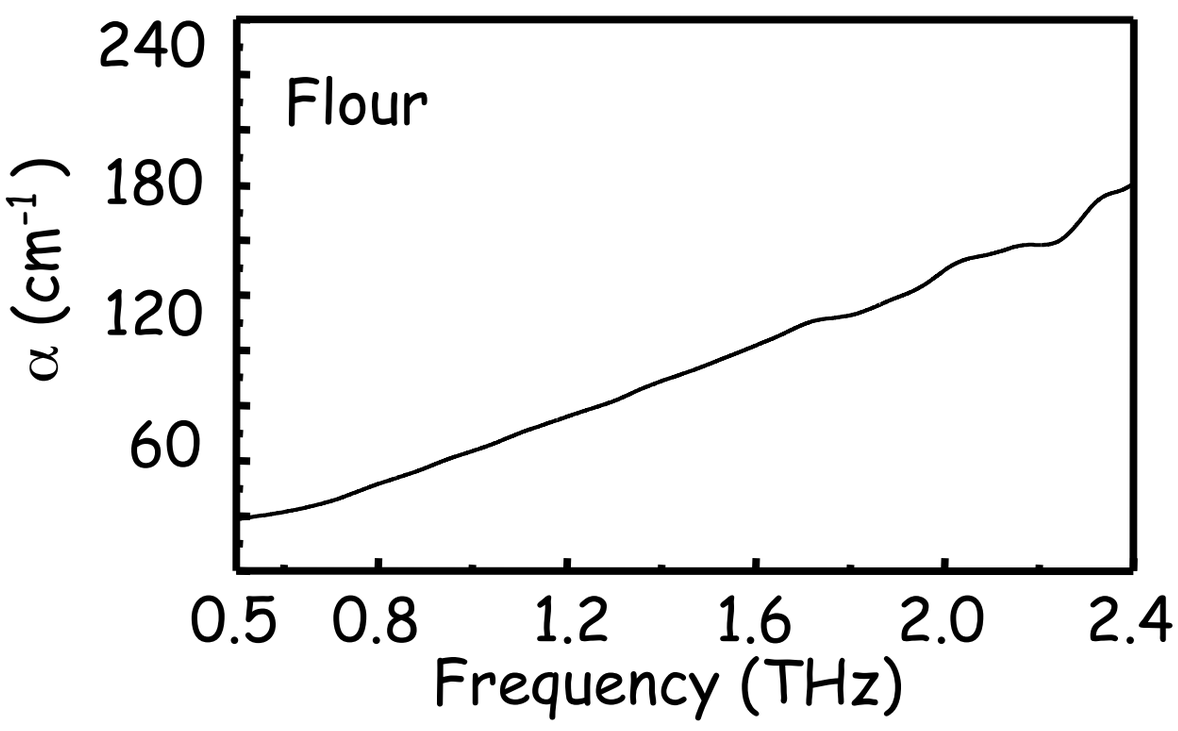


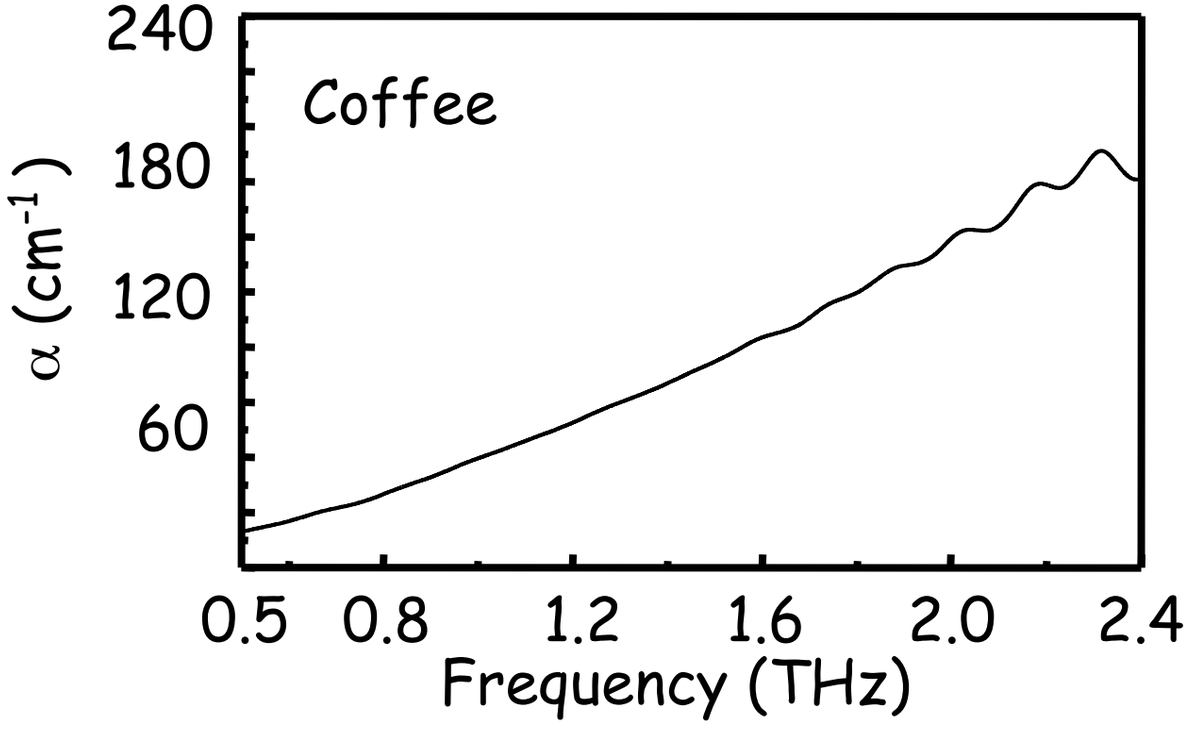
Kodo Kawase, RIKEN

Four Non-explosive Components









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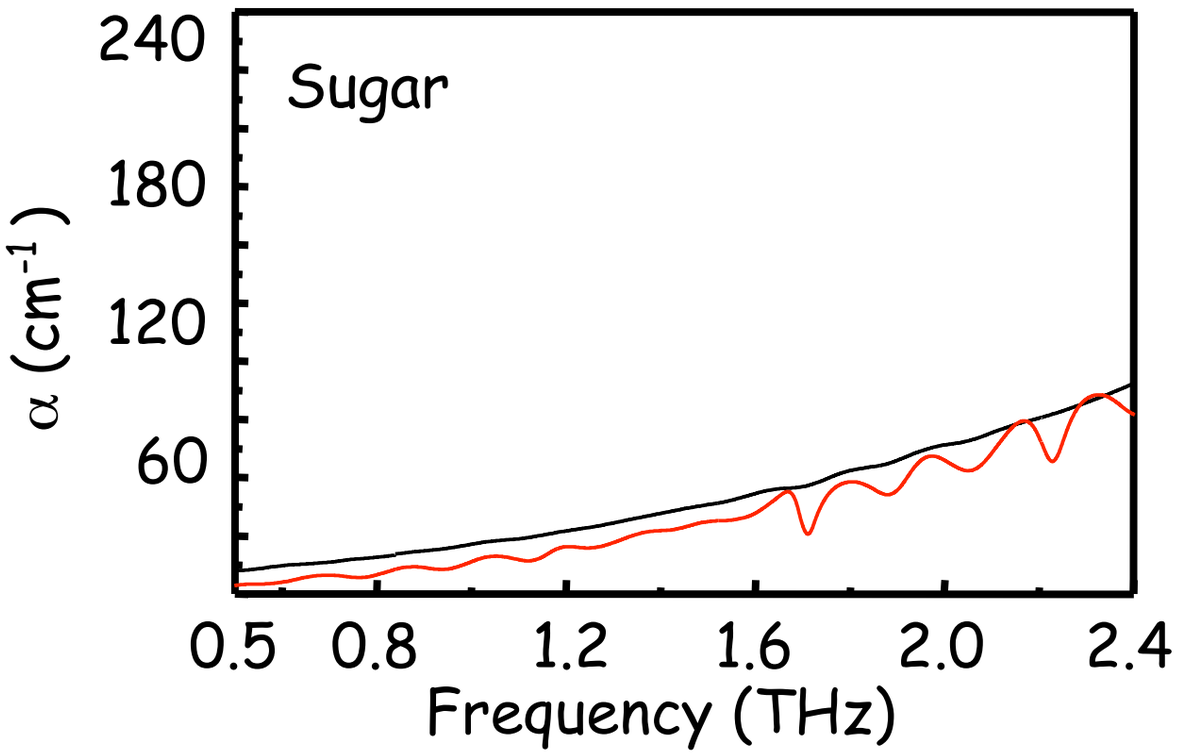
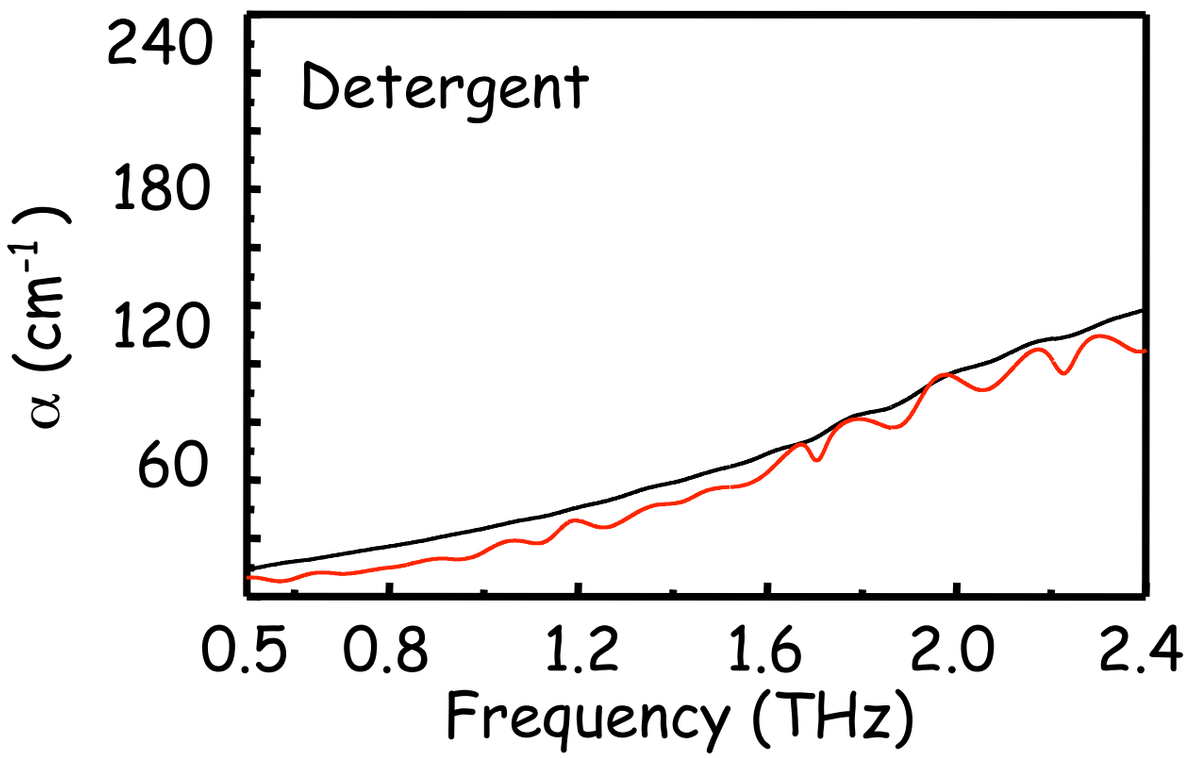
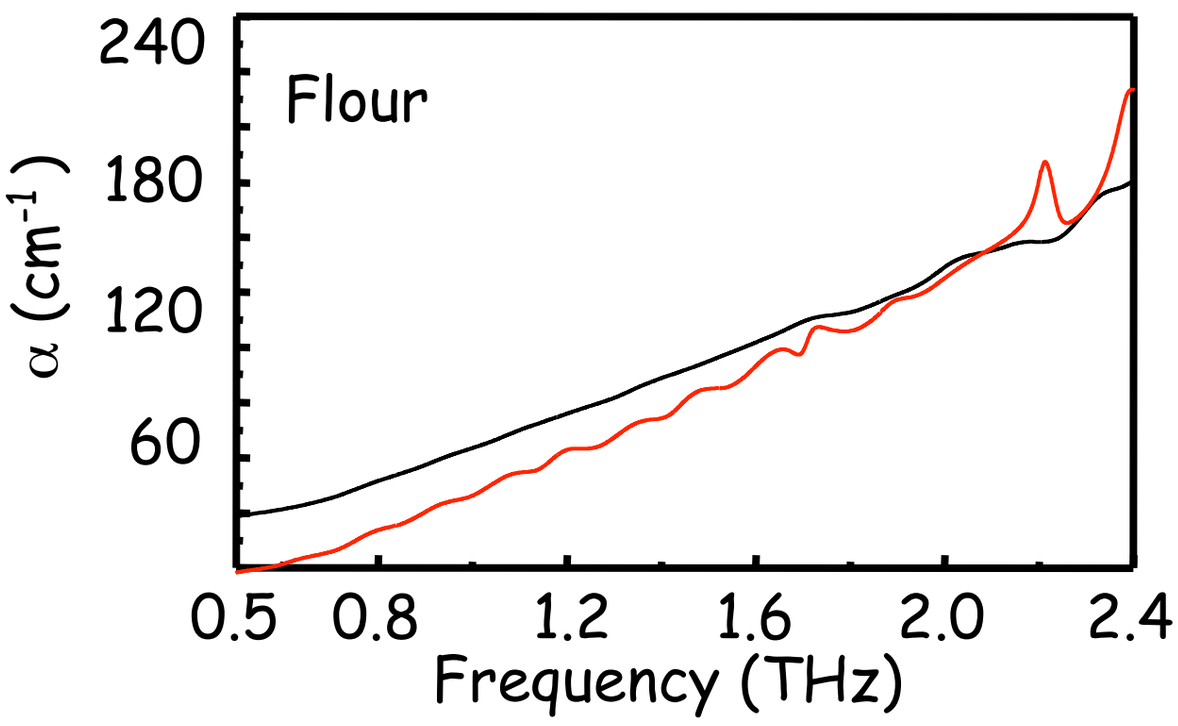
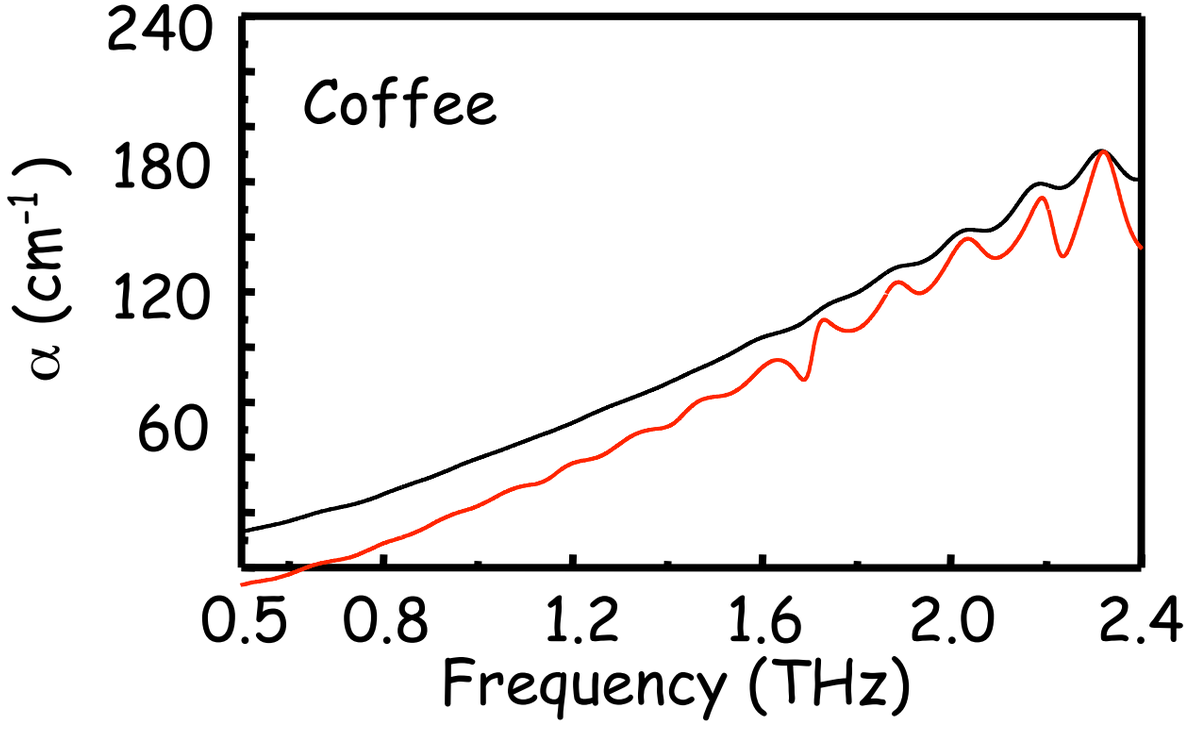
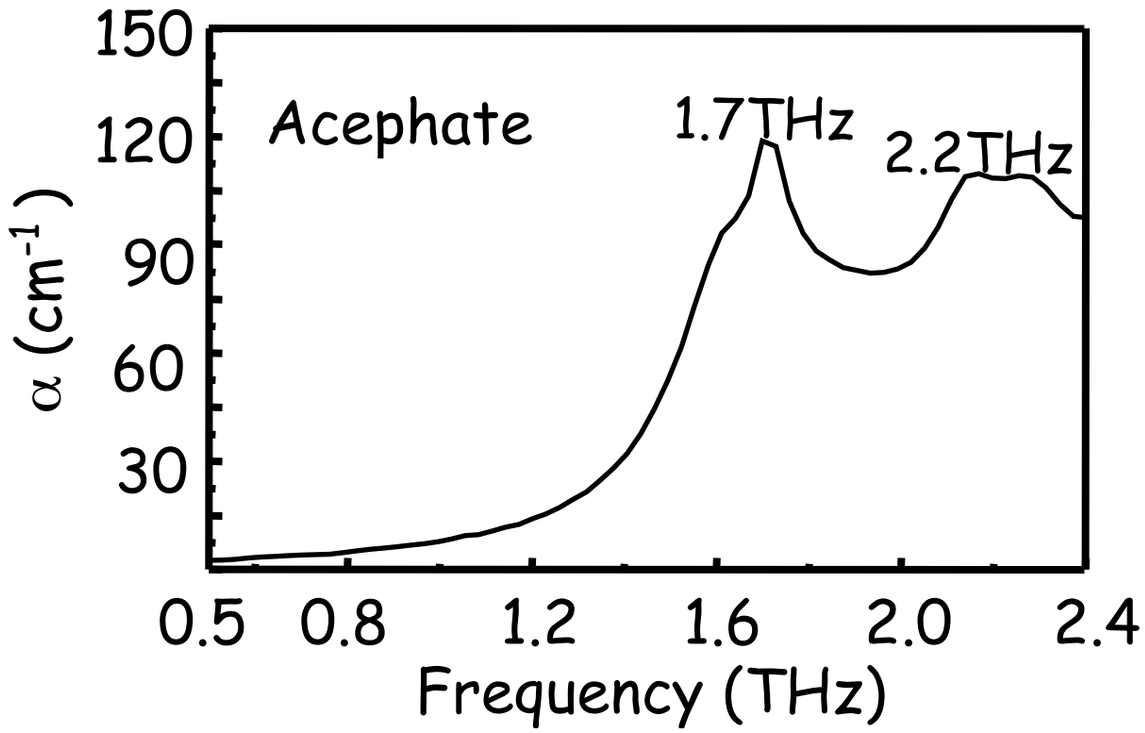


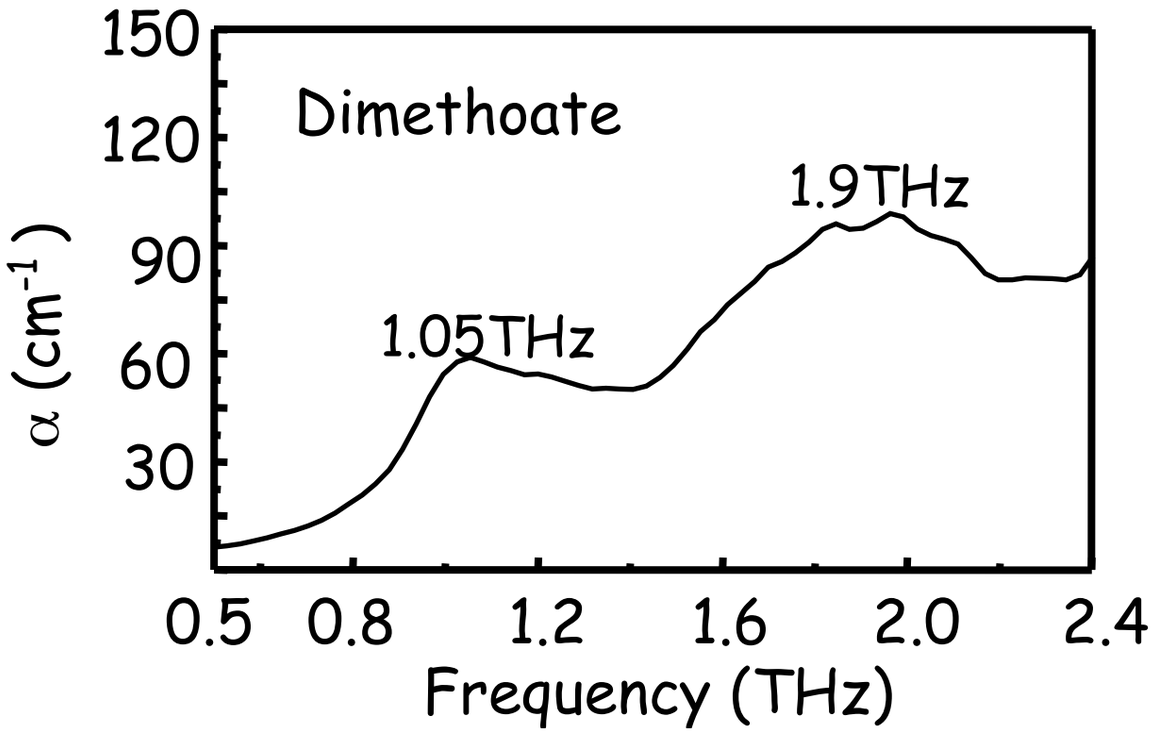


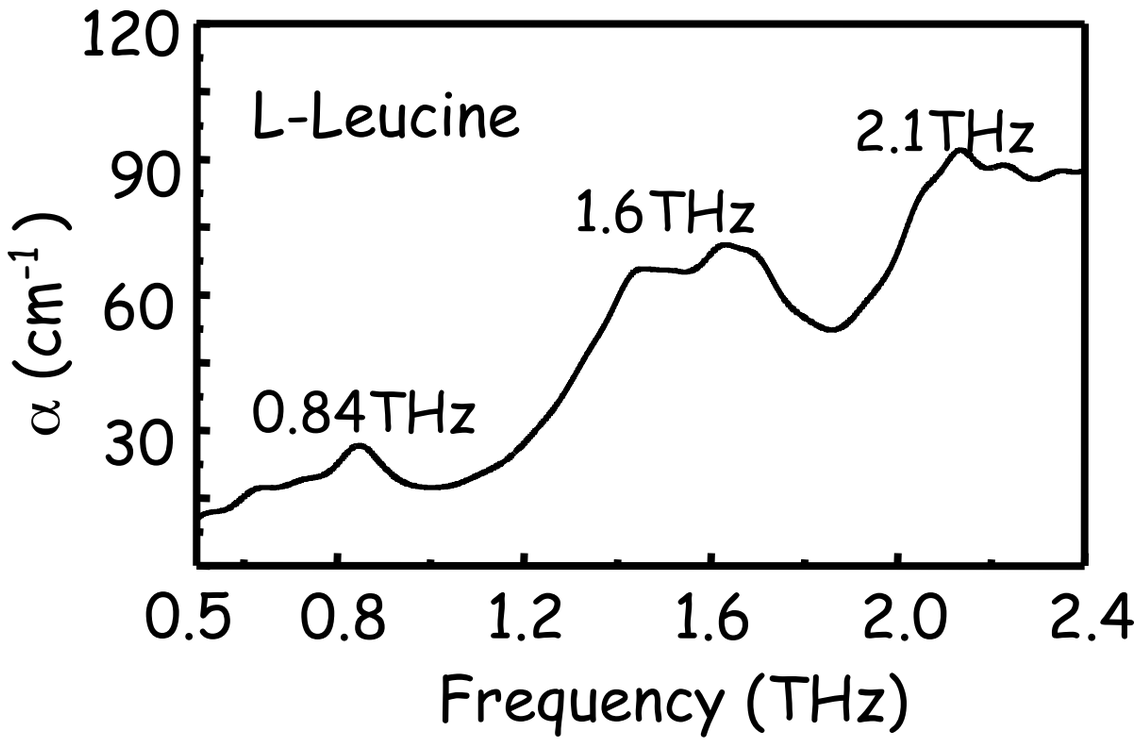


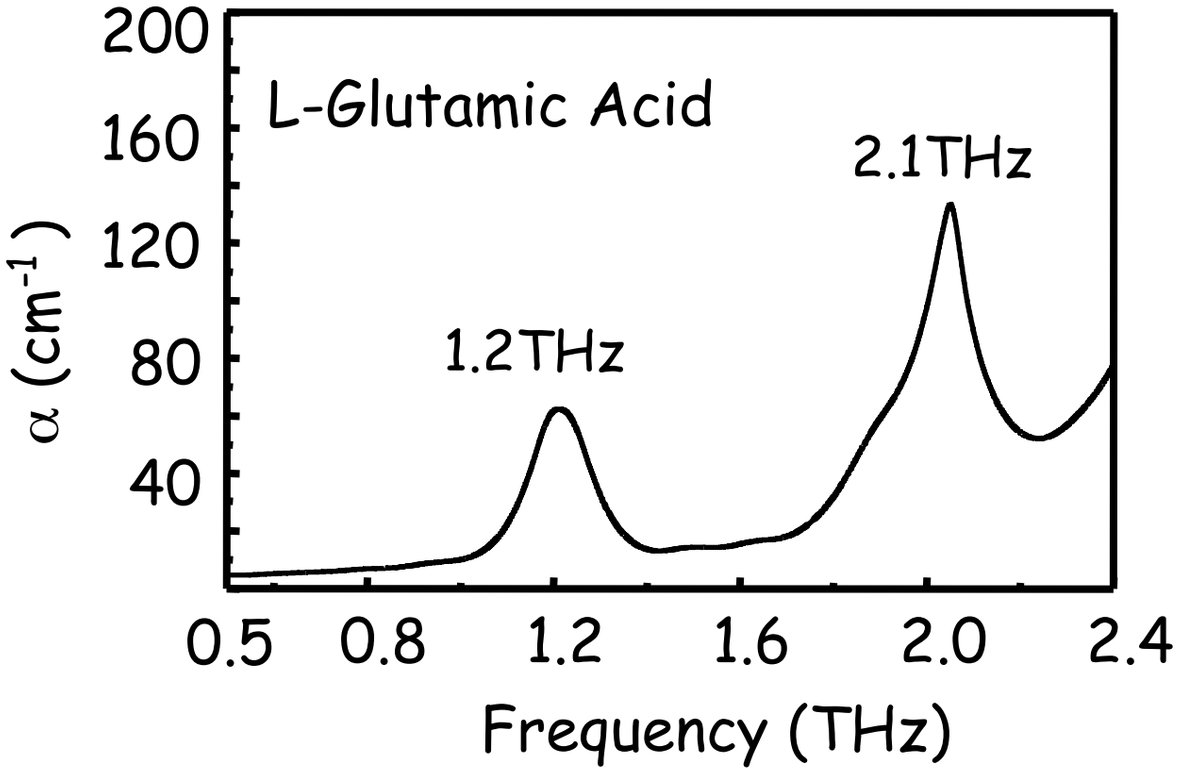


Pesticides and Bio-molecules



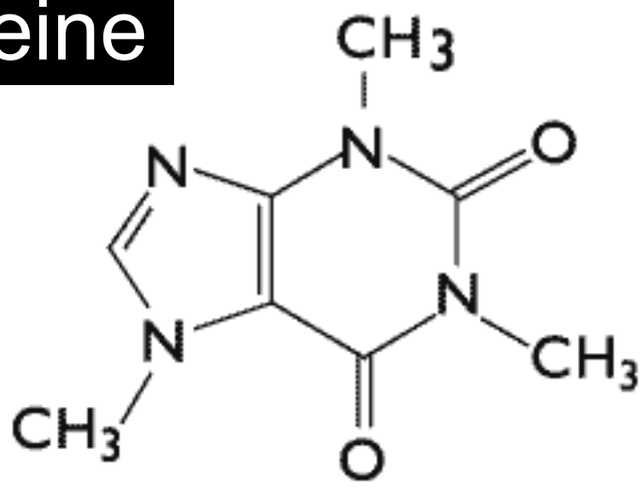




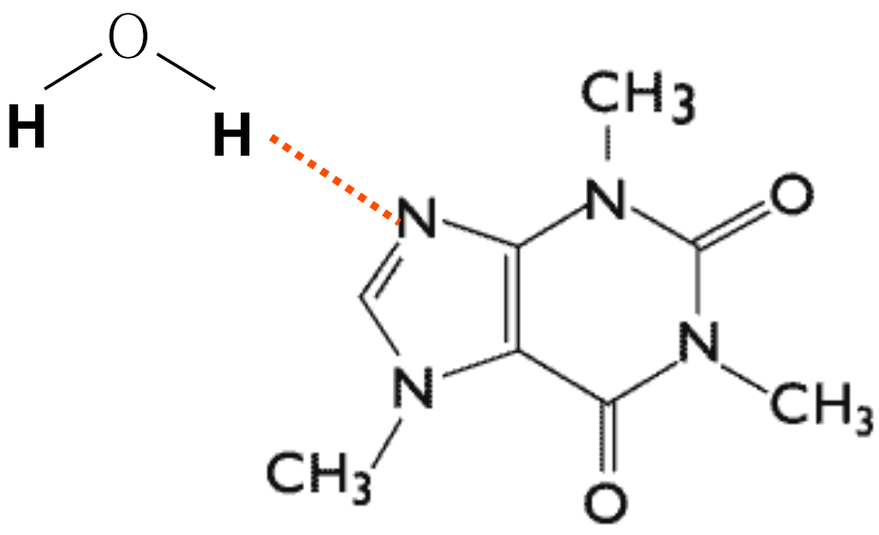


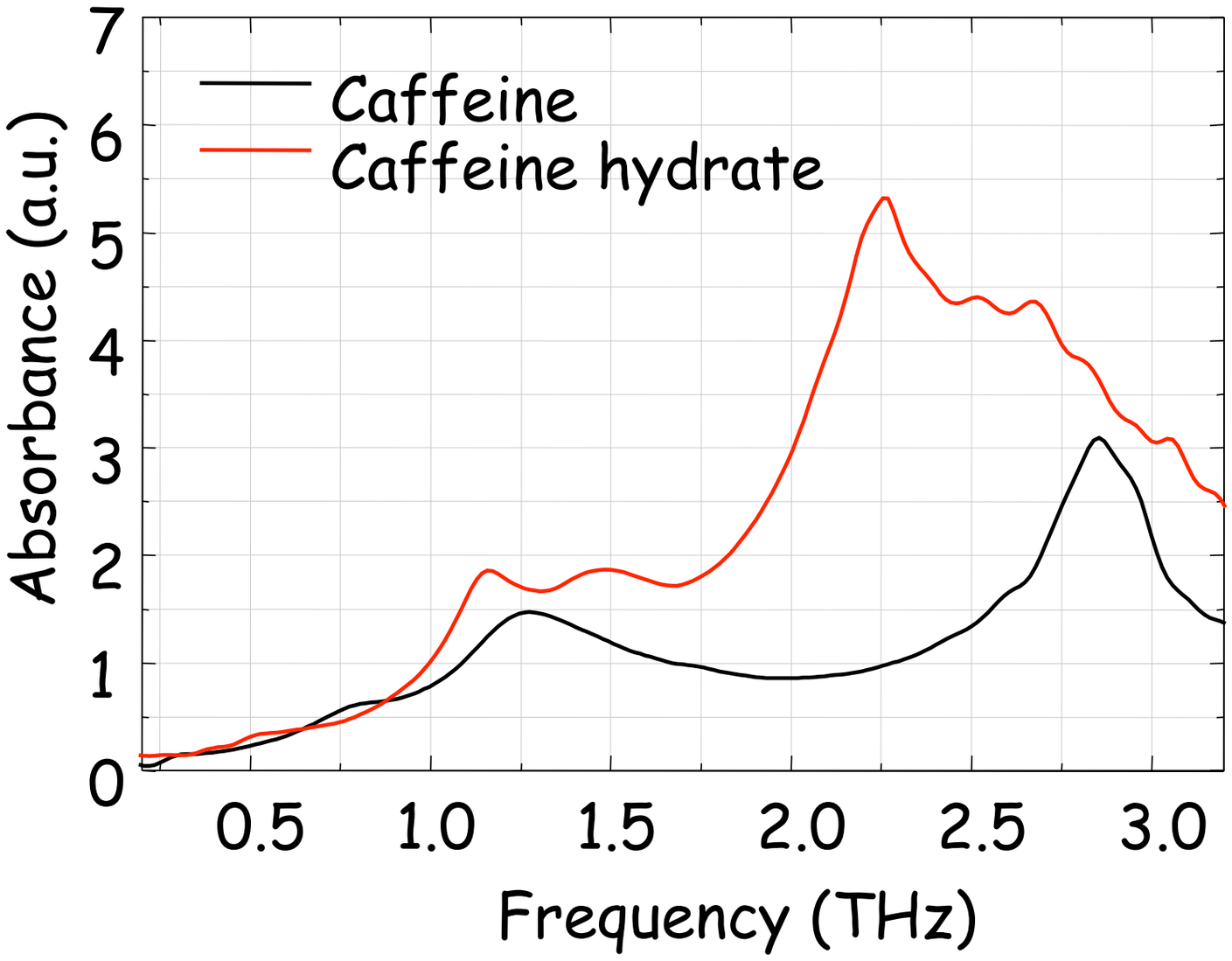
Distinguishing Anhydrous & Hydrated Drugs

Caffeine

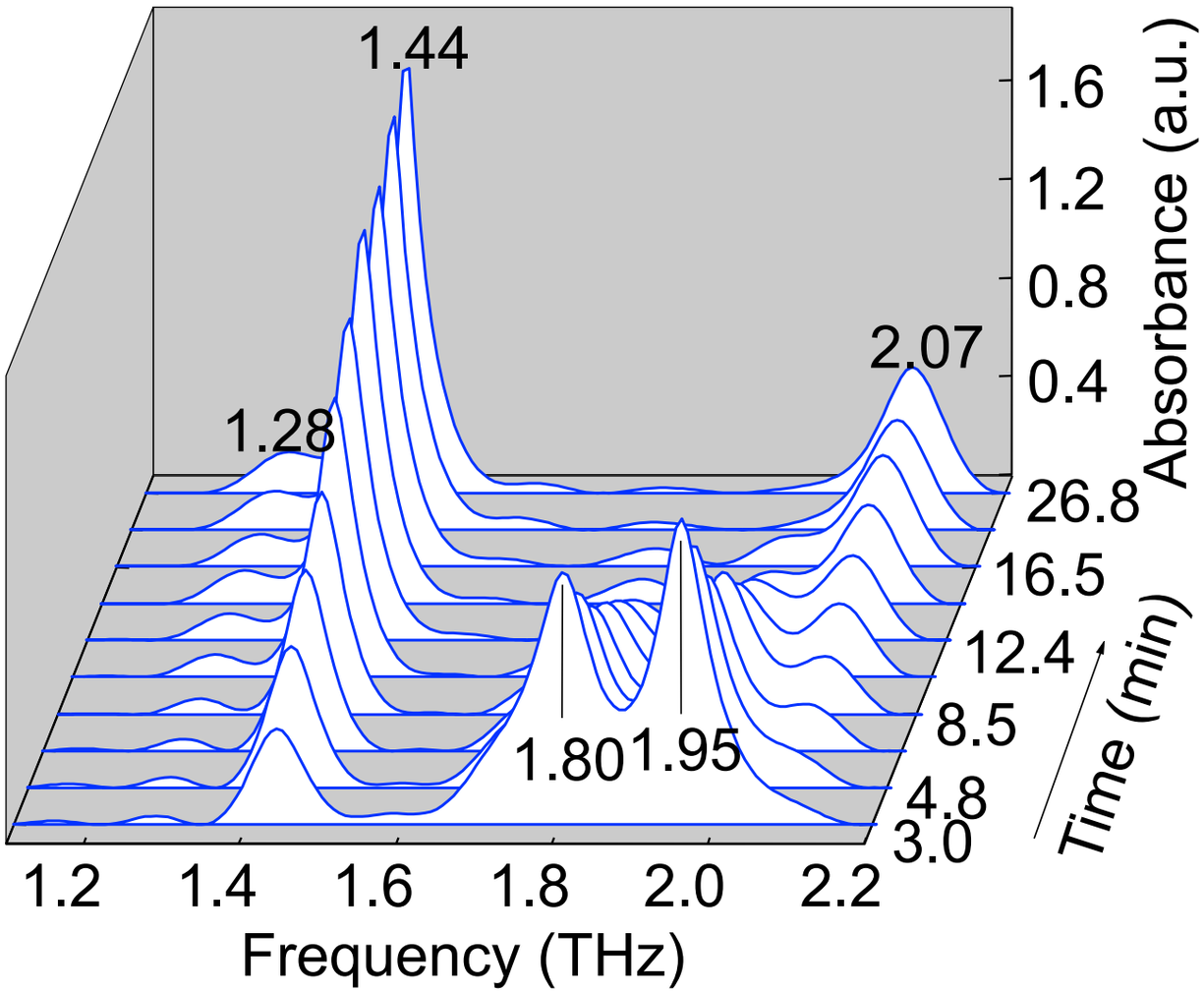


Hydrated Caffeine

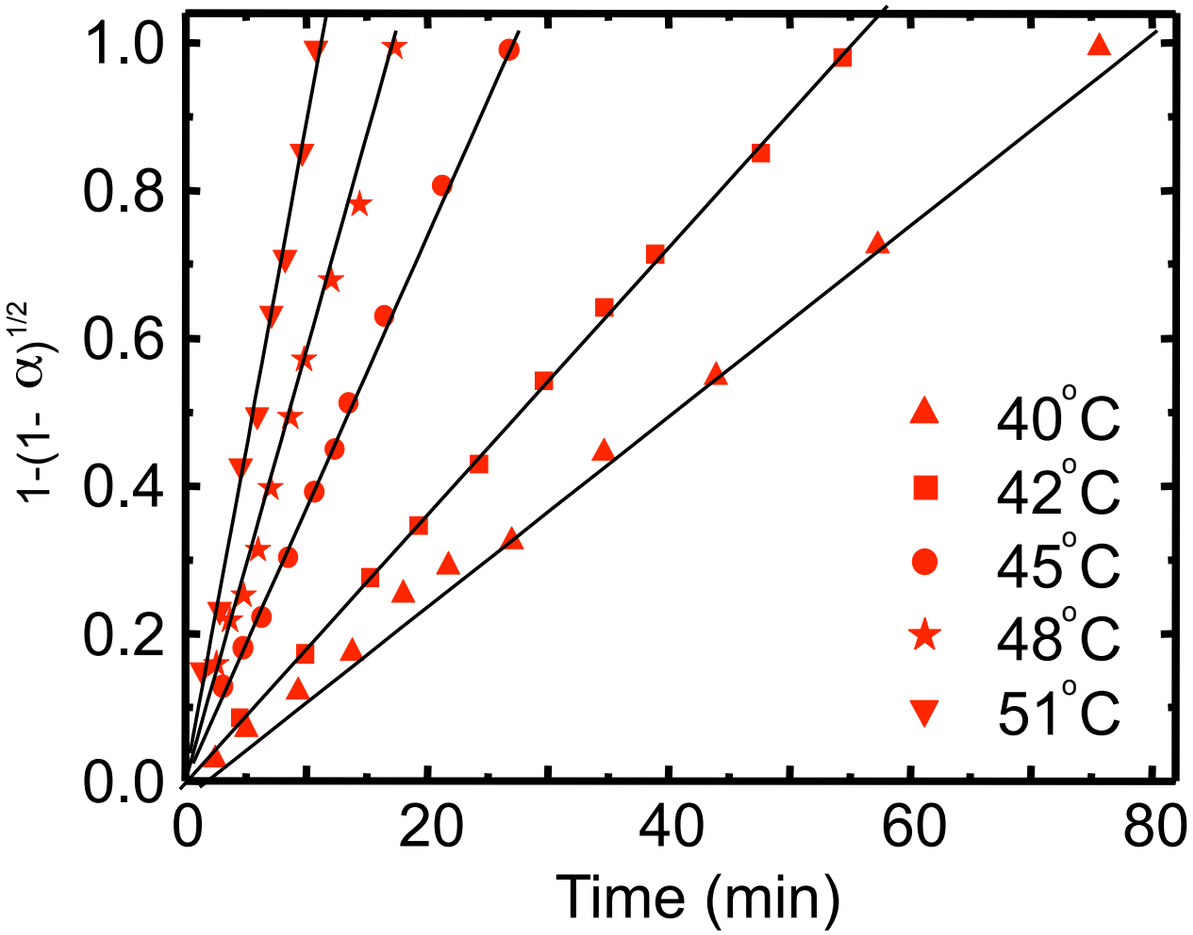




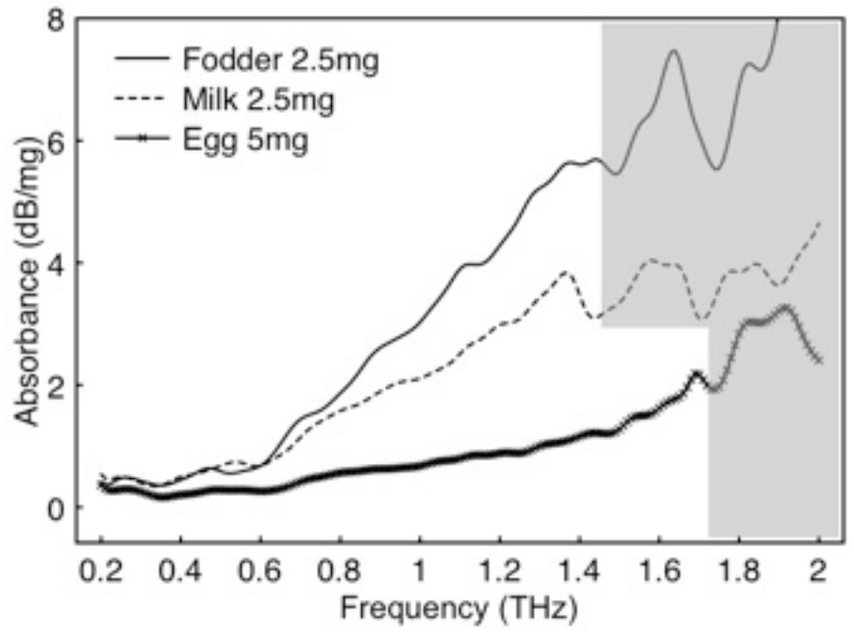
Dehydration of D-Glucose Monohydrate



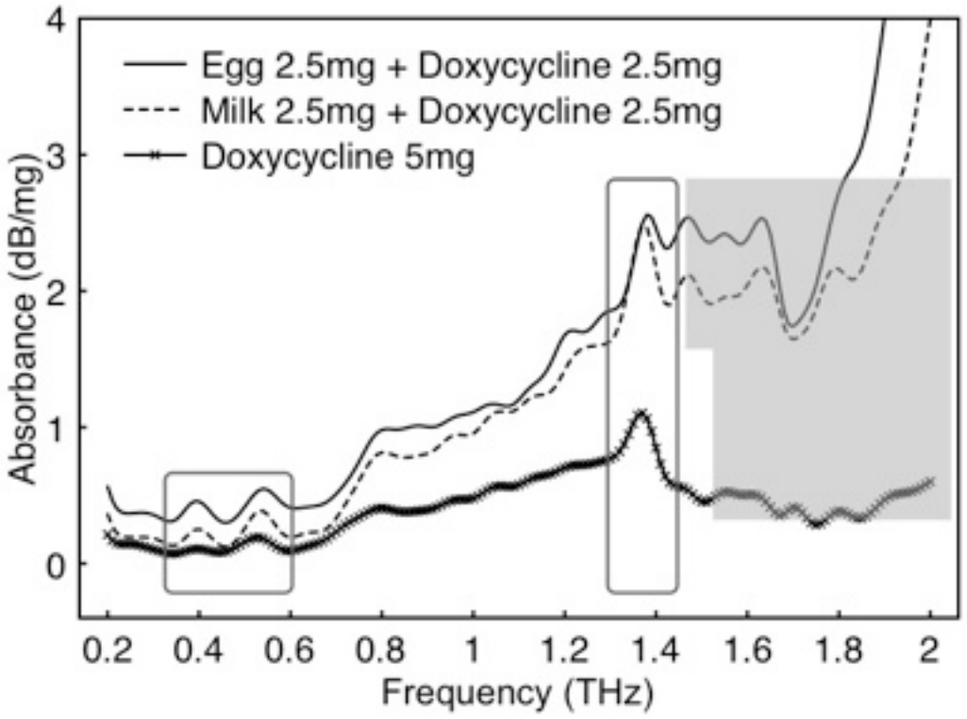
$$[-\ln(1-\alpha)]^{1/2} = kt$$

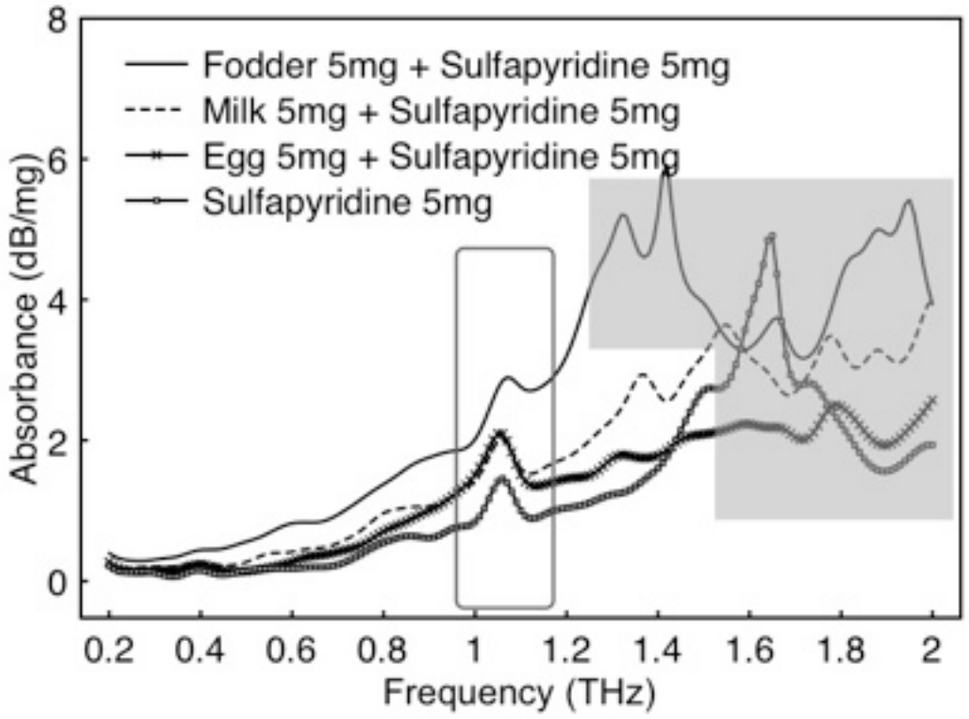


Antibiotics Identification



- ✓ Doxycycline and Sulfapyridine are antibiotics used to treat chickens grown for human consumption
- ✓ Antibiotics can be present in chicken derived products and mixtures
- ✓ Antibiotic fingerprints were identified in highly scattering food matrices (milk and egg powder, and fodder)
- ✓ Final application: detection of antibiotics in packaged foods





Courtesy of University of Barcelona

Instrument Detection Limit

- ✓ Relate SNR (dB) to minimum measurable absorbance

$$A_{\min}(f) = \ln\left[\left(\frac{E(f)}{E(f) - 3E_N(f)}\right)^2\right] = -2\ln\left[1 - 3\cdot 10^{-SNR_{dB}(f)/20}\right]$$

- ✓ Calculate minimum detectable material

*One-shot operating at 5 Hz

Sample	Peak Position	SNR (dB)*	Minimum Detectable	
			Absorbance	μg/cm²
α-Lactose	0.54 THz	38.06	0.0765	97.1
2HBP	0.69 THz	37.50	0.0817	25.8
RDX	0.82 THz	37.14	0.0852	24.5
2.4 DNT	1.09 THz	34.15	0.1213	35.2
L-Glutamic Acid	1.23 THz	32.04	0.1559	114
4HBAL	1.54 THz	24.08	0.4154	383

False Positive and Negative Rates

$$\text{False Negative Rate} = \frac{\text{Number of False Negatives}}{\text{Number of Positive Instances}}$$

$$\text{False Positive Rate} = \frac{\text{Number of False Positives}}{\text{Number of Negative Instances}}$$

False Positives vs. False Negatives
Which is more Important?

- ✓ Depends on Concept of Operations
- ✓ Explosives detection at airport ⟹ Minimize False Positives
- ✓ Contaminated Heparin ⟹ Minimize False Negatives

Statistical Results (5Hz)

	Correlation		PLS	
Sample	**FP Rate**	**FN Rate**	**FP Rate**	**FN Rate**
α-Lactose	0.0%	9.8%	0.0%	11.0%
2HBP	0.0%	0.5%	0.0%	7.3%
PABA	17.9%	23.2%	0.0%	51.7%
RDX	3.0%	20.6%	0.0%	32.5%
2,4-DNT	0.0%	0.0%	0.0%	2.7%
L-Glutamic Acid	0.0%	1.5%	0.2%	43.2%
NG	1.4%	12%	8.2%	1.8%
4HBAL	1.7%	0.4%	0.4%	2.4%

1600 measurements at 5Hz – Pressed Pellets, Transmission Mode with mini-Z 3.0

Statistical Results (1Hz)

	Correlation		PLS	
Sample	**FP Rate**	**FN Rate**	**FP Rate**	**FN Rate**
α-Lactose	0.0%	0.5%	0.0%	9.5%
2HBP	0.0%	0.0%	0.0%	7.5%
PABA	0.0%	7.8%	0.0%	32.8%
RDX	0.9%	0.0%	0.0%	3.5%
2,4-DNT	0.3%	0.0%	0.0%	2.0%
L-Glutamic Acid	0.0%	1.9%	0.4%	1.0%
NG	0.1%	1.5%	2.0%	11.1%
4HBAL	0.4%	0.3%	0.4%	0.0%

1600 measurements at 1Hz – Pressed Pellets, Transmission Mode with mini-Z 3.0

Contingency Table (5Hz)

	Control										
	RDX	C4	Comp B	PE4	Detasheet	Semtex-A	Semtex-H	Tetryl	NG	Total	False Positive Rate
RDX	**608**	180	241	15	0	0	0	0	0	1044	**41.8%**
C4	0	**397**	8	3	1	0	0	0	0	409	**2.9%**
Comp B	0	0	**0**	0	0	0	0	0	0	0	**N/A**
PE4	0	0	170	**567**	0	0	6	0	0	743	**23.7%**
Detasheet	0	0	0	11	**160**	0	44	0	0	215	**25.6%**
Semtex-A	0	0	0	0	117	**563**	30	0	0	710	**20.7%**
Semtex-H	0	0	0	0	0	0	**137**	0	0	137	**0.0%**
Tetryl	0	0	0	0	0	0	0	**486**	0	486	**0.0%**
NG	0	0	0	0	4	0	5	1	**520**	530	**1.9%**
N/A	3	21	183	5	290	39	228	114	81	964	
Total	611	598	602	601	572	602	450	601	601	5238	
False Negative Rate	**0.5%**	**33.6%**	**100.0%**	**5.6%**	**72.0%**	**6.5%**	**69.6%**	**19.1%**	**13.5%**		

Contingency Table (1Hz)

	RDX	C4	Comp B	PE4	Detasheet	Semtex-A	Semtex-H	Tetryl	NG	HMX	TNT	Total	False Positive Rate
RDX	**234**	60	60	4	0	0	0	0	0	0	0	358	**34.6%**
C4	0	**174**	2	0	0	0	0	0	0	0	0	176	**1.1%**
Comp B	0	0	**0**	0	0	0	0	0	0	0	0	0	**N/A**
PE4	0	0	172	**230**	0	0	0	0	0	0	1	403	**42.9%**
Detasheet	0	0	0	0	**178**	0	36	0	0	0	0	214	**16.8%**
Semtex-A	0	0	0	0	36	**232**	21	0	0	5	0	294	**21.1%**
Semtex-H	0	0	0	0	0	0	**117**	0	0	0	0	117	**0.0%**
Tetryl	0	0	0	0	0	0	0	**229**	0	0	1	230	**0.4%**
NG	0	0	0	0	0	0	0	0	**234**	0	0	234	**0.0%**
HMX	0	0	0	0	0	0	31	0	0	**177**	0	208	**14.9%**
TNT	0	0	0	0	0	0	0	0	0	0	**80**	80	**0.0%**
N/A	0	0	0	0	20	2	26	5	0	52	121	226	
Total	234	234	234	234	234	234	231	234	234	234	203	2540	
False Negative Rate	**0.0%**	**25.6%**	**100.0%**	**1.7%**	**23.9%**	**0.9%**	**49.4%**	**2.1%**	**0.0%**	**32.2%**	**60.6%**		

Instrumentation Overview

Zomega Terahertz Corporation

Mini-Z Terahertz Time-Domain Spectrometer

- Portable, compact, and integrated design
- Turn-key operation (no alignment, no complex setup)
- Waveform rate up to 500 Hz (high speed model)
- Transmission and reflection geometries
- Vibration tolerant
- Open architecture
- Options: attenuated total reflection (ATR), θ–2θ reflection, imaging

Micro-Z THz Time-Domain Spectrometer

- Compact THz transceiver
- Fast scanning up to 500 Hz
- Real-time spectroscopy
- Broadband sensitivity up to 2 THz
- Transmission and reflection geometries
- Built-in spectral library and identification software

Micro-Z Clip


ZOMEGA
TERAHERTZ
micro-Z Handheld Terahertz Spectrometer

Thank You!

Questions?

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