



National Technical University of Athens  
School of Applied Mathematical and Physical sciences



**Terahertz detection**

**of harmful residues in honey**

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 **COST** TD1102

**PHOTOTECH: BIOSENSORS & BIOCHIPS**  
21<sup>st</sup>-25<sup>th</sup> October 2013 , Athens , Greece

## Motivation

*Food quality and safety control as a tool for regulatory enforcement, protection of consumer's life, health and safety.*

### Current analytical methods (few of them...)

- High-performance liquid chromatography (HPLC)
- Gas chromatography (GC)
- mass spectrometry (MS)
- nuclear magnetic resonance (NMR)
- infrared spectroscopy (IR)
- Fluorescence spectroscopy
- Electrochemical (including also biosensors here), and so forth.

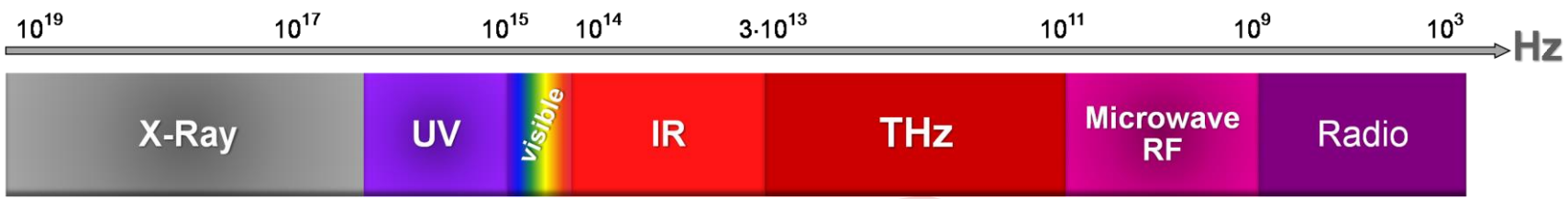


### New methods for food analysis and inspection:

- rapid
- portable (increase of testing capacity)
- non-destructive
- with no need of food pre-treatment
- real-time testing on the production line

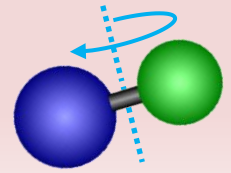


# Terahertz radiation

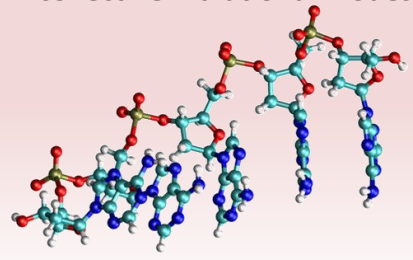


$\lambda \sim 10\mu\text{m} - 3\text{mm}$   
 $h\nu \sim 120 - 0.413 \text{ meV}$

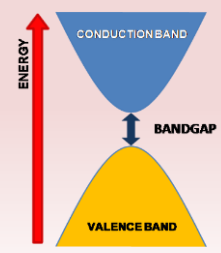
Molecular rotations



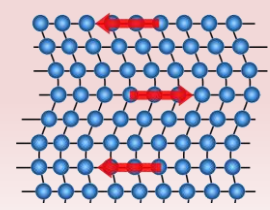
Hydrogen Bonds, Torsions, collective vibrational modes



Superconductivity gap



Lattice phonons



Imaging





# Terahertz radiation

- ❑ Non-ionizing/invasive radiation
- ❑ Transparent to non-conducting materials (paper, wood, plastic, etc.)
- ❑ High sensitivity to water
- ❑ Fingerprint spectrum: low-frequency torsional and vibrational motion of molecules

## Imaging

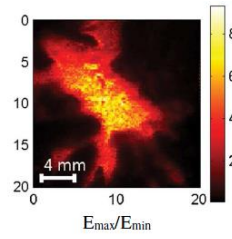
Security



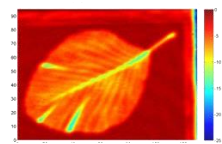
Drugs and explosives



Medical- Cancer



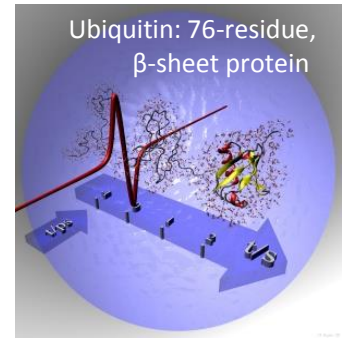
Plant stress



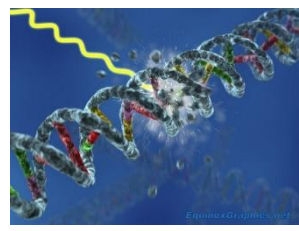
Leaf in visible after cutting | Leaf in THz after cutting

## THz pump/probe

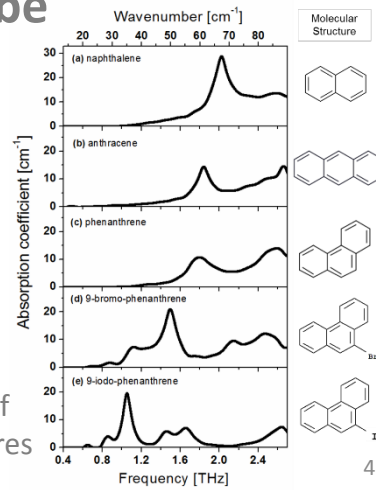
Protein folding



DNA damage or repair



Discrimination of molecular structures

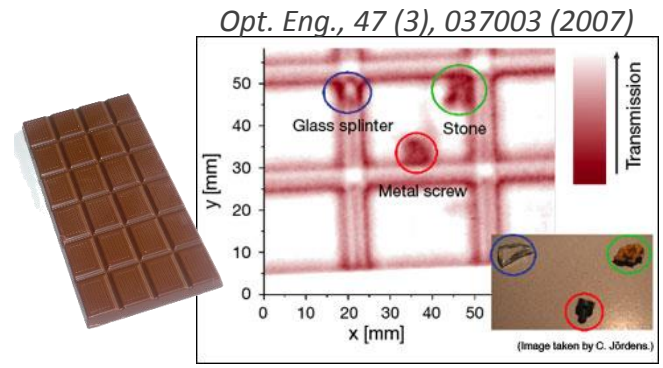




# THz radiation and Food industry

- Non-ionizing/invasive radiation
- Transparent to non-conducting materials (paper, wood, plastic, etc.)
- High sensitivity to water
- Fingerprint spectrum: low-frequency torsional and vibrational motion of molecules

## ❖ Detection of foreign bodies in food

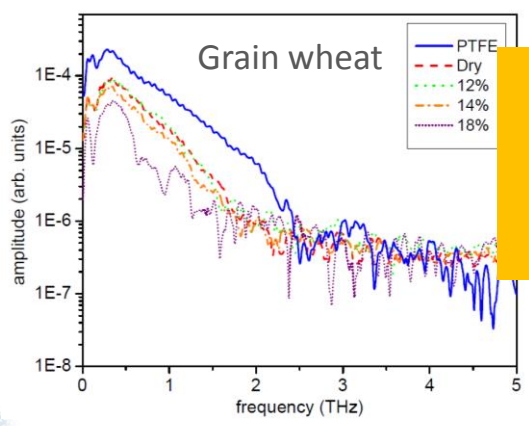


## ❖ Detection of Antibiotics/ pesticides (in milk, egg powders, rice, dried tomato)

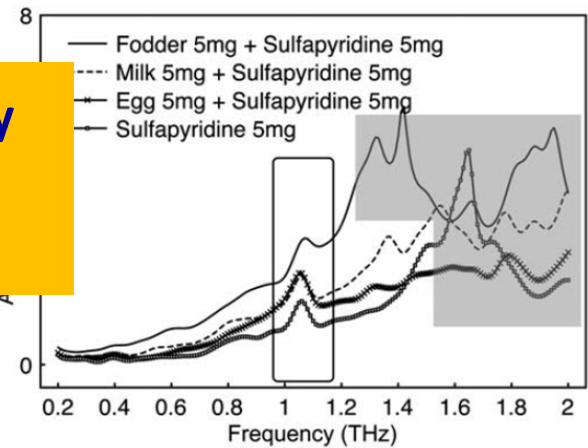
*Appl. Spectr. Rev., 48, 439 (2013)*  
*Analyst, 136, 1733 (2012)*  
*IEEE Trans., 58, 7, 2064 (2010)*

## ❖ Moisture detection

*J Infrar. Milli. Terahz. Waves. 33, 97 (2012)*



**THz and Food industry**  
**More to be done!!!**





# Food industry: Honey



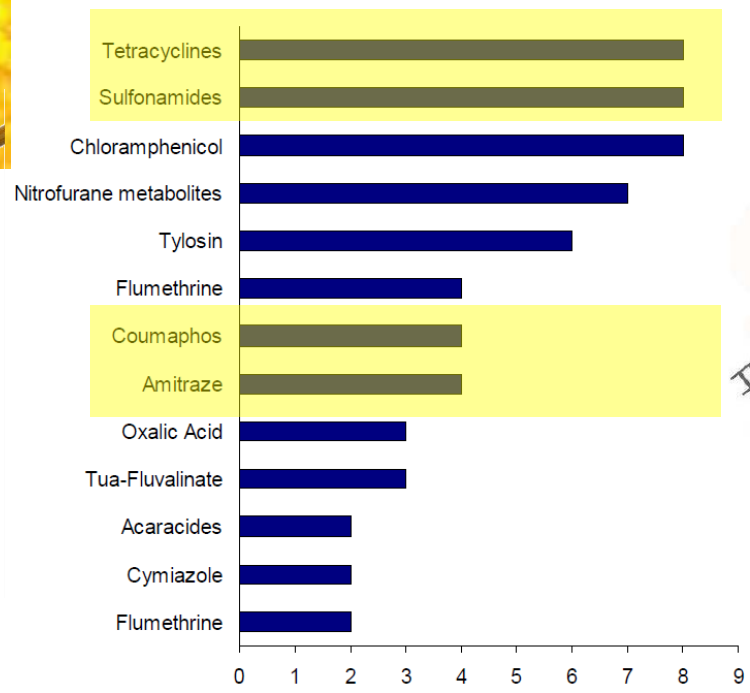
**Honey: Natural and healthy product.....**

**.....Polluted via different sources of contamination**  
(mainly to improper use of beekeeping practices)

**Need:** novel detection technologies rapid, non-destructive able to determine the presence of multi-residues in honey.



Contamination parameters

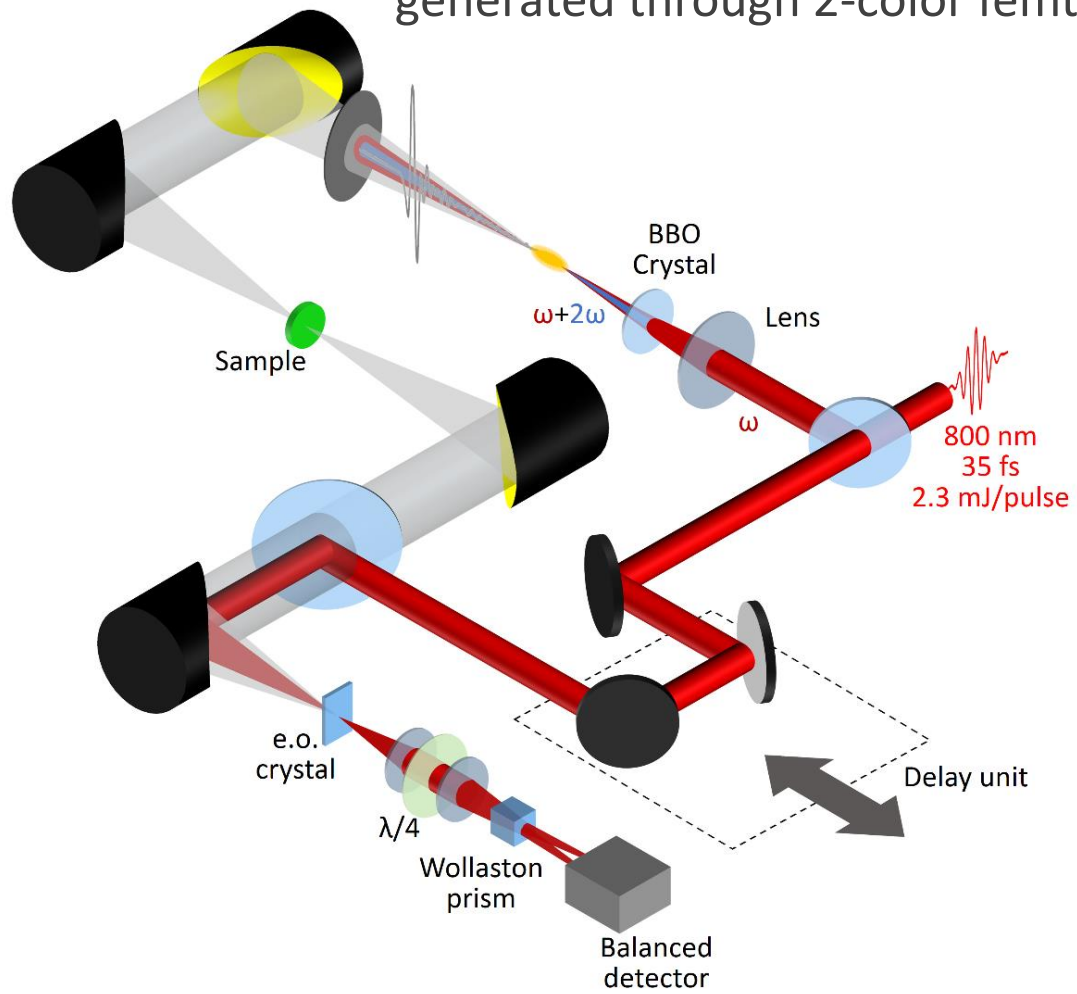


Real-time detection

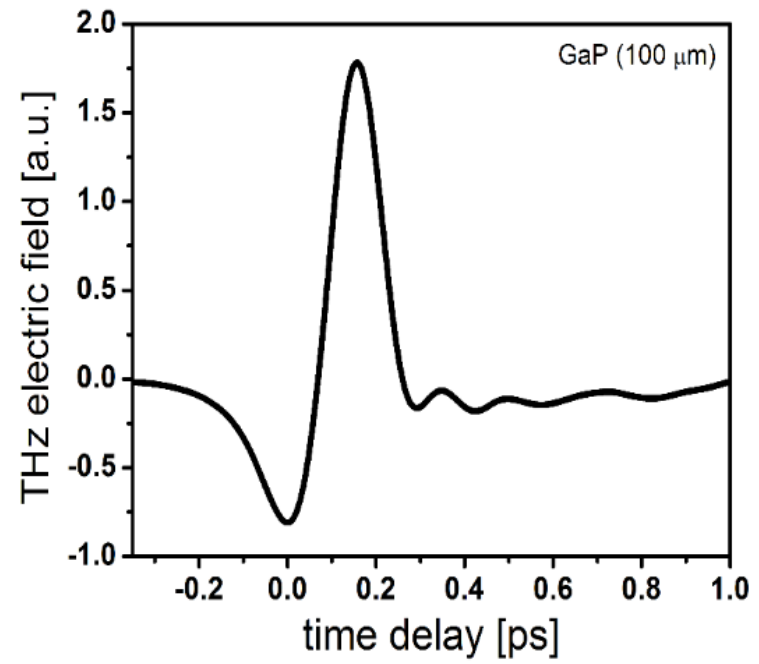


# Terahertz source

**THz source:** Broadband (~0.1-35 THz), intense THz pulses (200 kV/cm) generated through 2-color femtosecond laser filaments in air.

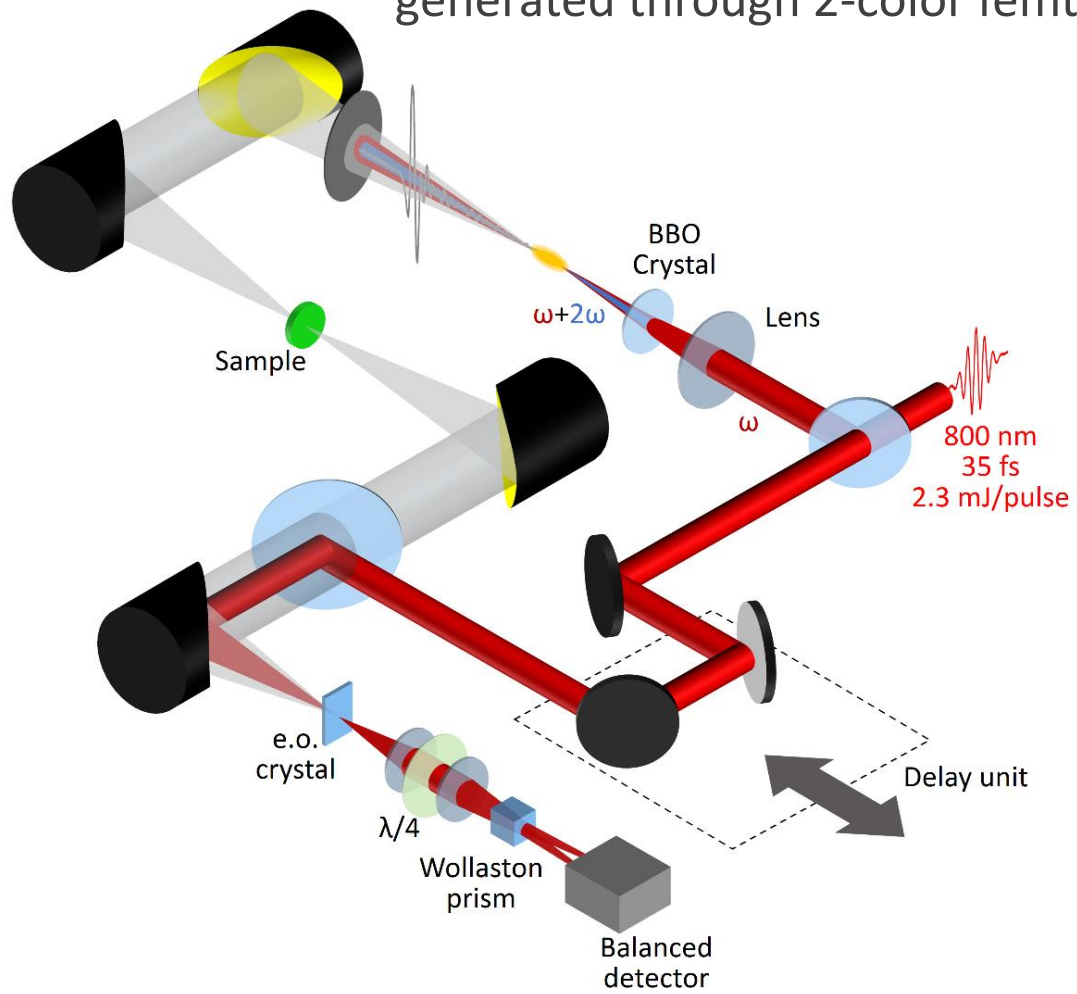


Coherent detection in time domain of the THz electric field.



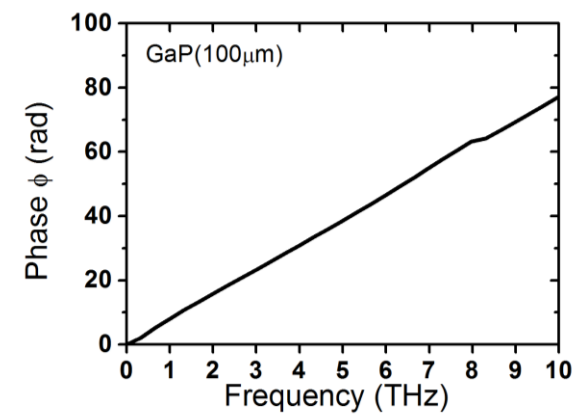
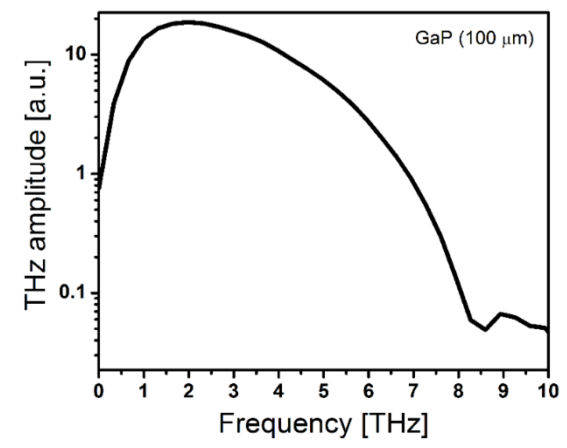
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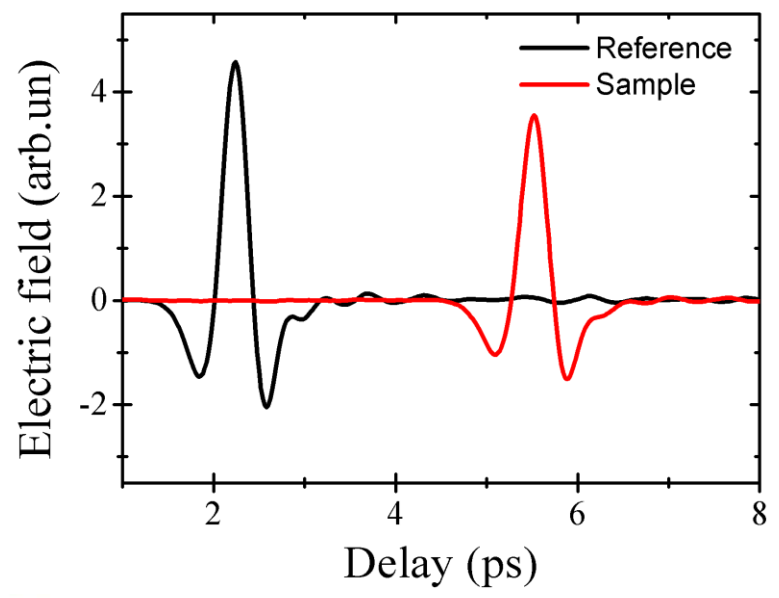
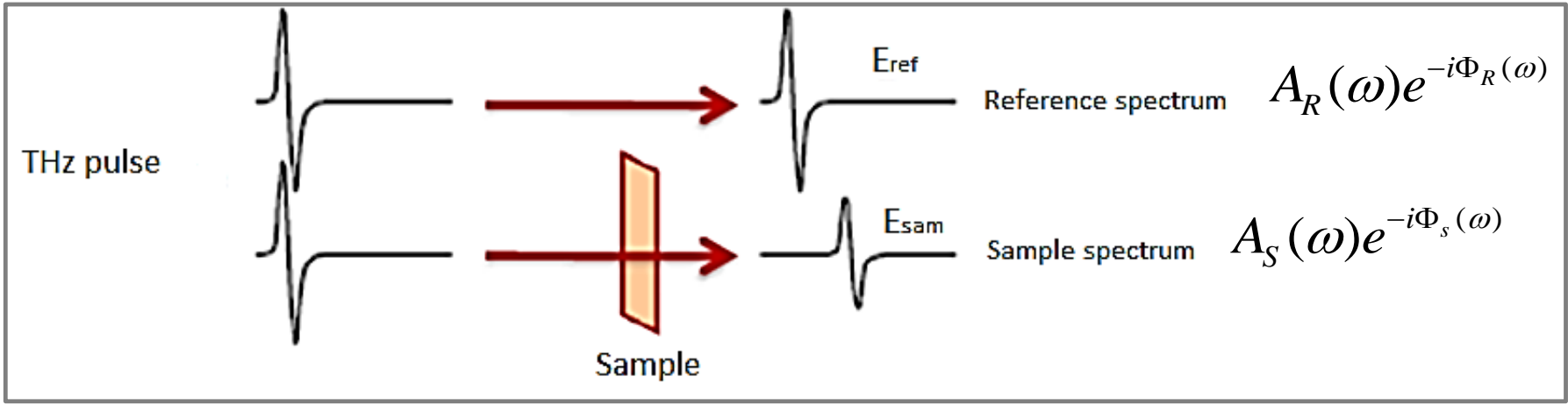
Fourier transform the time signal

$$\tilde{E}(\omega) \equiv A(\omega)e^{-i\Phi(\omega)} = \int dt E(t)e^{-i\omega t}$$





# THz time-domain spectroscopy (THz-TDS)



Refractive index  $n = 1 + \frac{[\Phi_S(\omega) - \Phi_R(\omega)]c}{\omega d}$

Absorption coefficient:  $a = -\frac{2}{d} \ln \left( \frac{A_S(\omega)}{A_R(\omega)} \cdot T \right)$

$$T = \frac{(n(\omega) + 1)^2}{4n(\omega)}$$

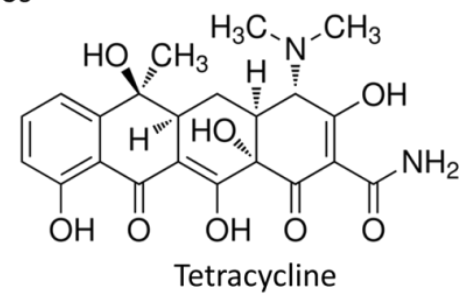
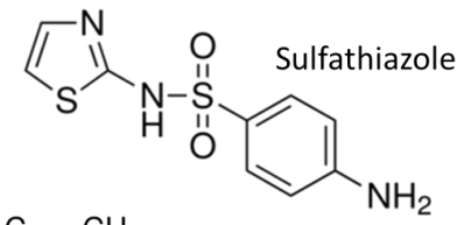
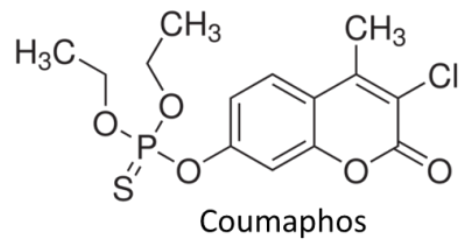
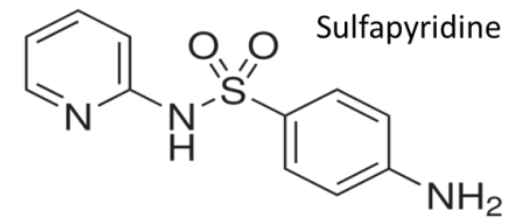


# THz spectra: Antibiotics & Acaricides

**PELLETS:** mixture of HDPE powder + chemical compound

- Concentration 20% w/w
- Thickness ~1 mm
- Diameter 7 mm
- Weight 40 mg

<b>Antibiotics</b>	<input type="checkbox"/> Sulfapyridine <input type="checkbox"/> Sulfathiazole <input type="checkbox"/> Tetracycline
<b>Acaricides</b>	<input type="checkbox"/> Coumaphos <input type="checkbox"/> Amitraz



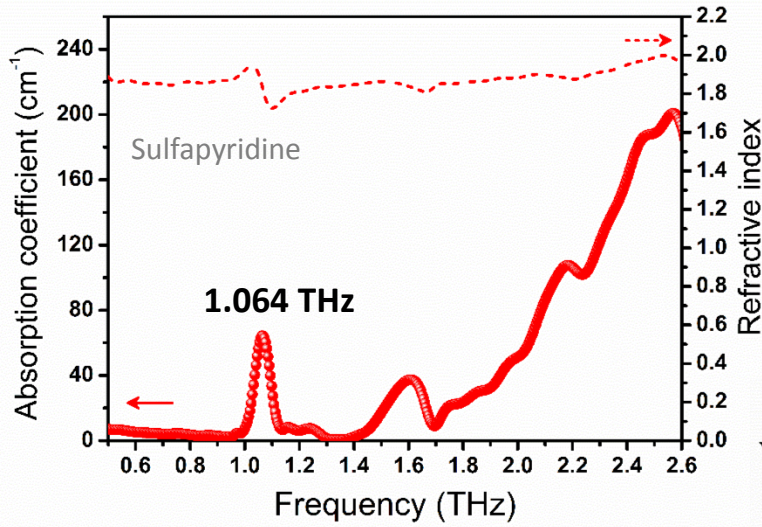
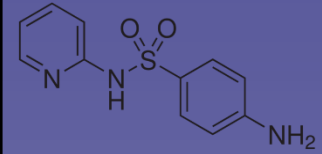
**SAMPLE HOLDER**  
(pellets)



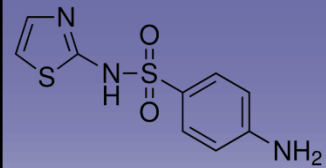


# THz spectra : Antibiotics

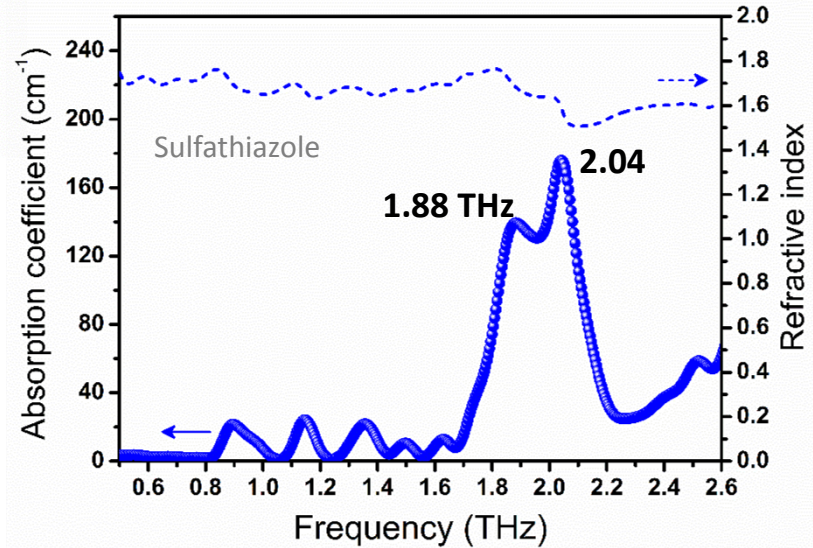
## Sulfapyridine



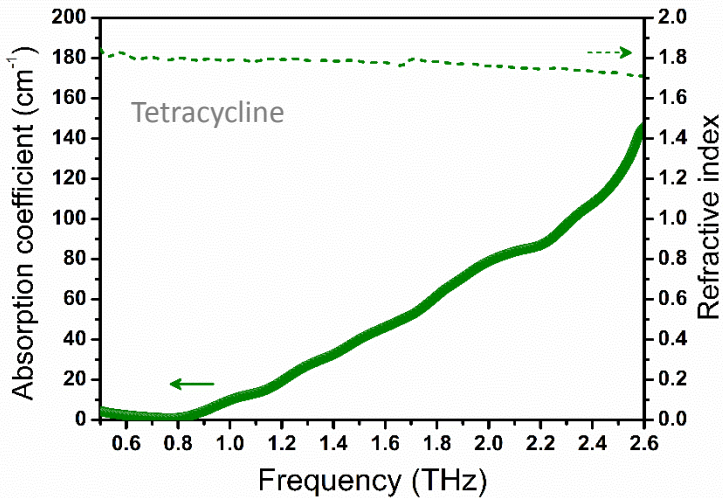
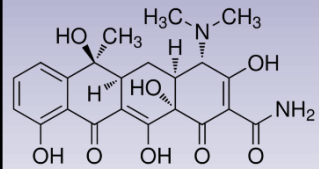
## Sulfathiazole



Distinct resonance peaks in the THz regime



## Tetracycline



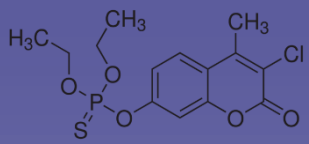


# THz spectra : Acaricides

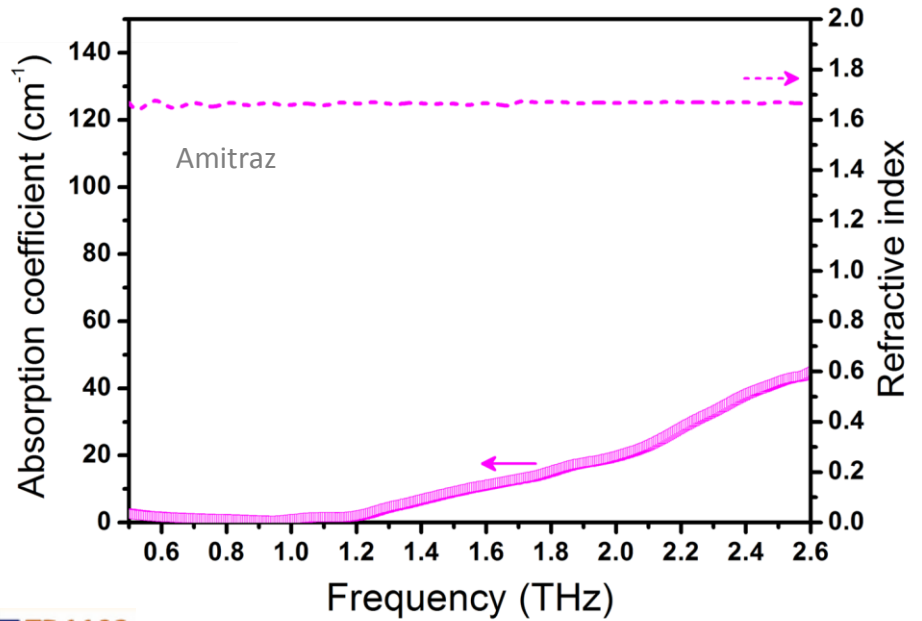
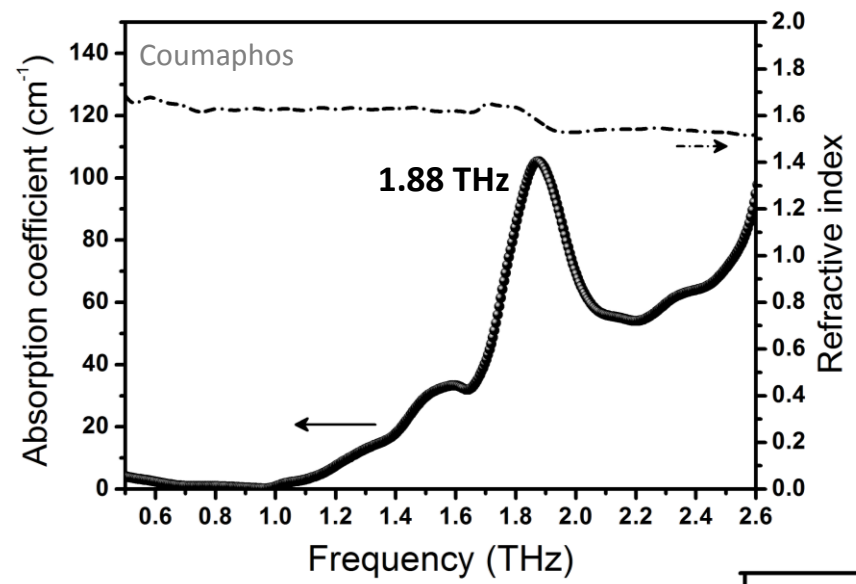
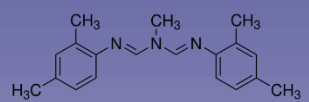
THz region (0.5-2.6 THz)

Massaouti et al. J. Appl. Spectr. (2013)

## Coumaphos



## Amitraz



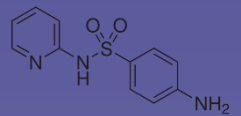
**Distinct resonance peaks (0.5-2.6 THz)**  
 ↓  
**Discrimination of:**

- Sulfapyridine
- Sulfathiazole
- Coumaphos

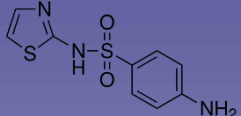


# THz spectra : Antibiotics

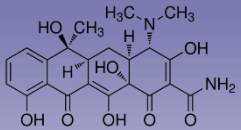
## Sulfapyridine



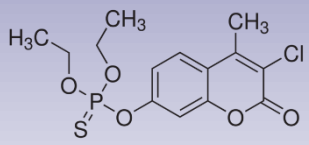
## Sulfathiazole



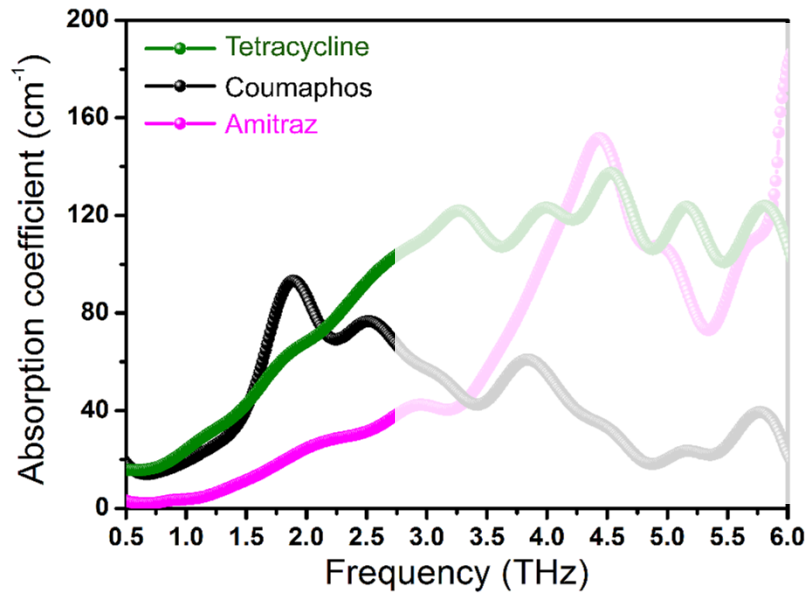
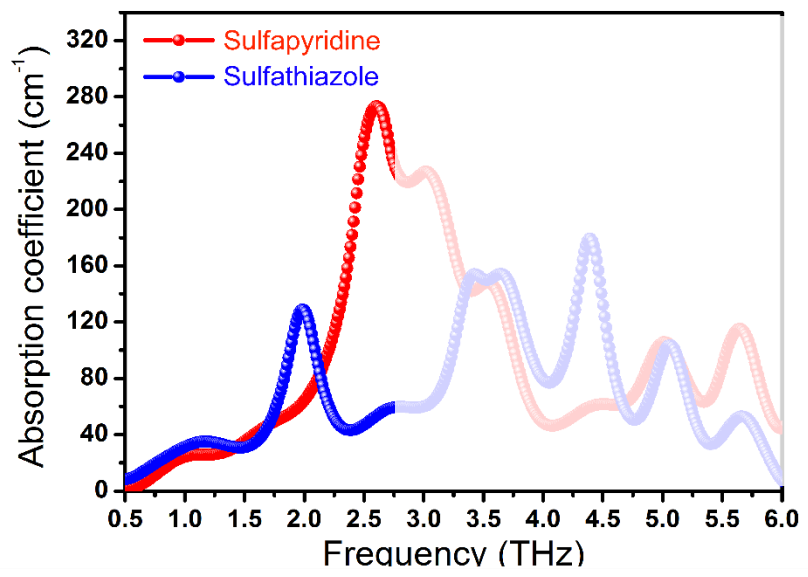
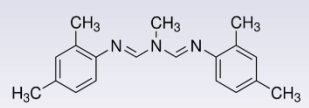
## Tetracycline



## Coumaphos



## Amitraz



Detection in a wider THz region  
0.5-6.0 THz

↓

Additional resonance peaks

↓

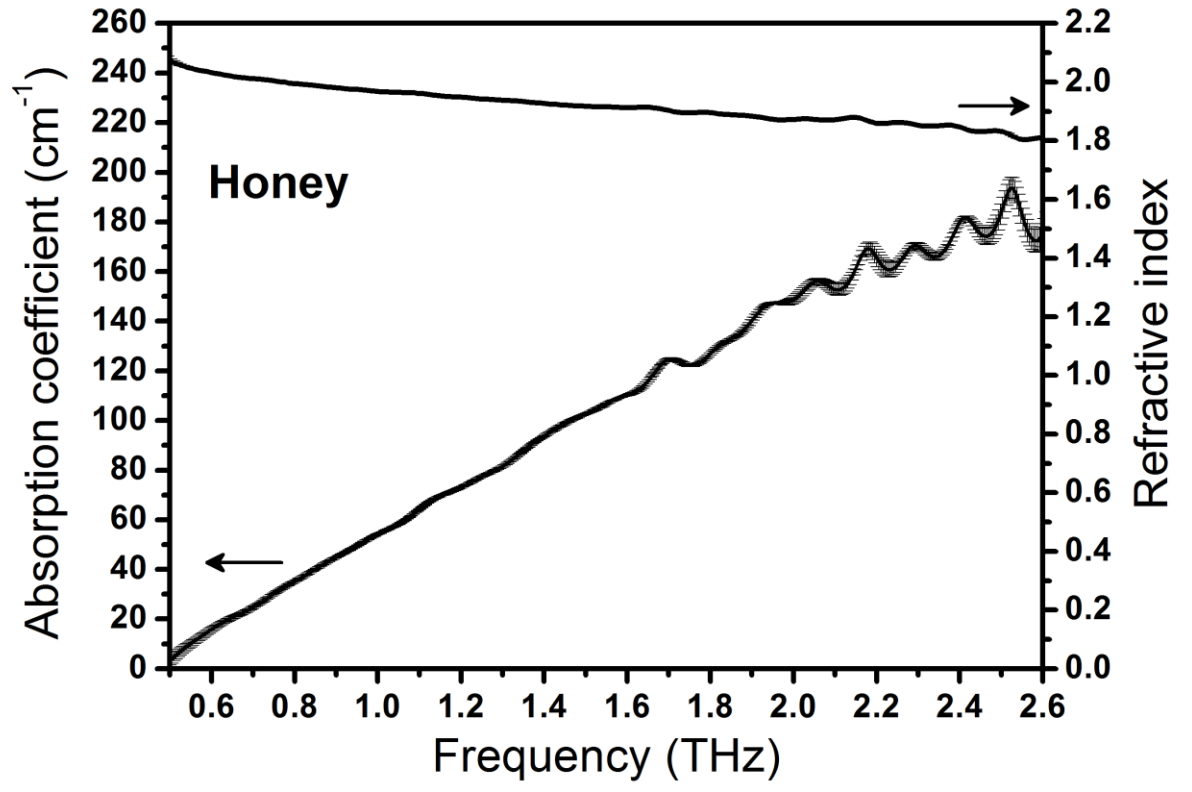
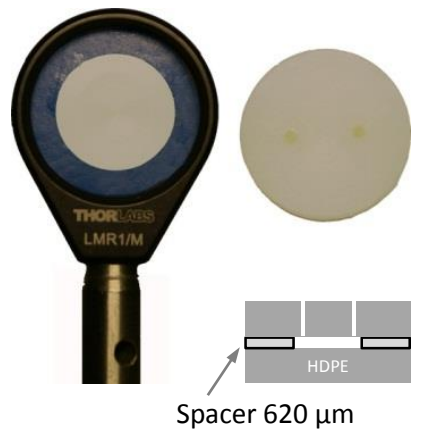
Discrimination of:

- Sulfapyridine
- Sulfathiazole
- Coumaphos
- Amitraz

# THz spectrum of honey

Massaouti et al. J. Appl. Spectr. (2013)

## SAMPLE HOLDER (liquids)



Highly absorptive:  $\alpha = 50 \text{ cm}^{-1}$  (1 THz)

Refractive index:  $n = 1.8$

# Sulfapyridine in honey

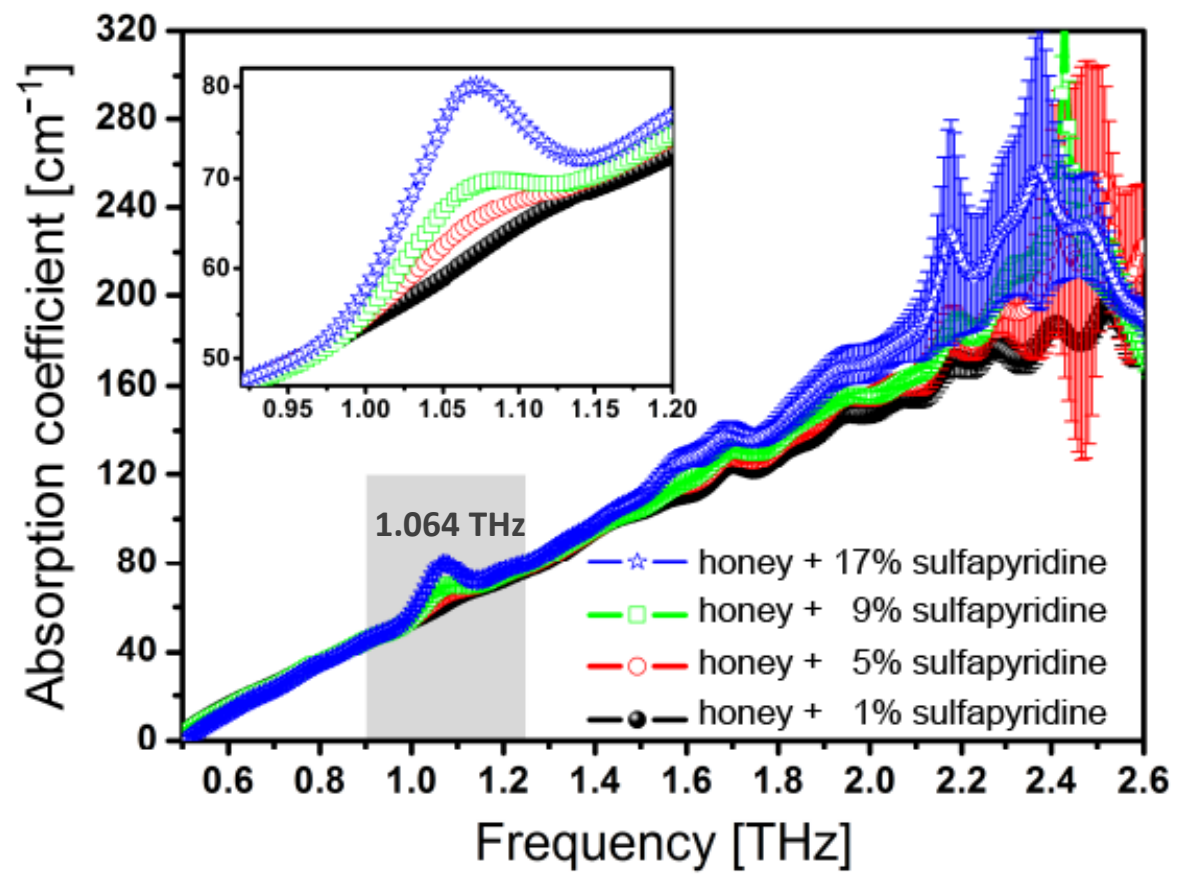
## SAMPLE HOLDER (liquids)



## Mixture:



different concentrations  
(w/w)



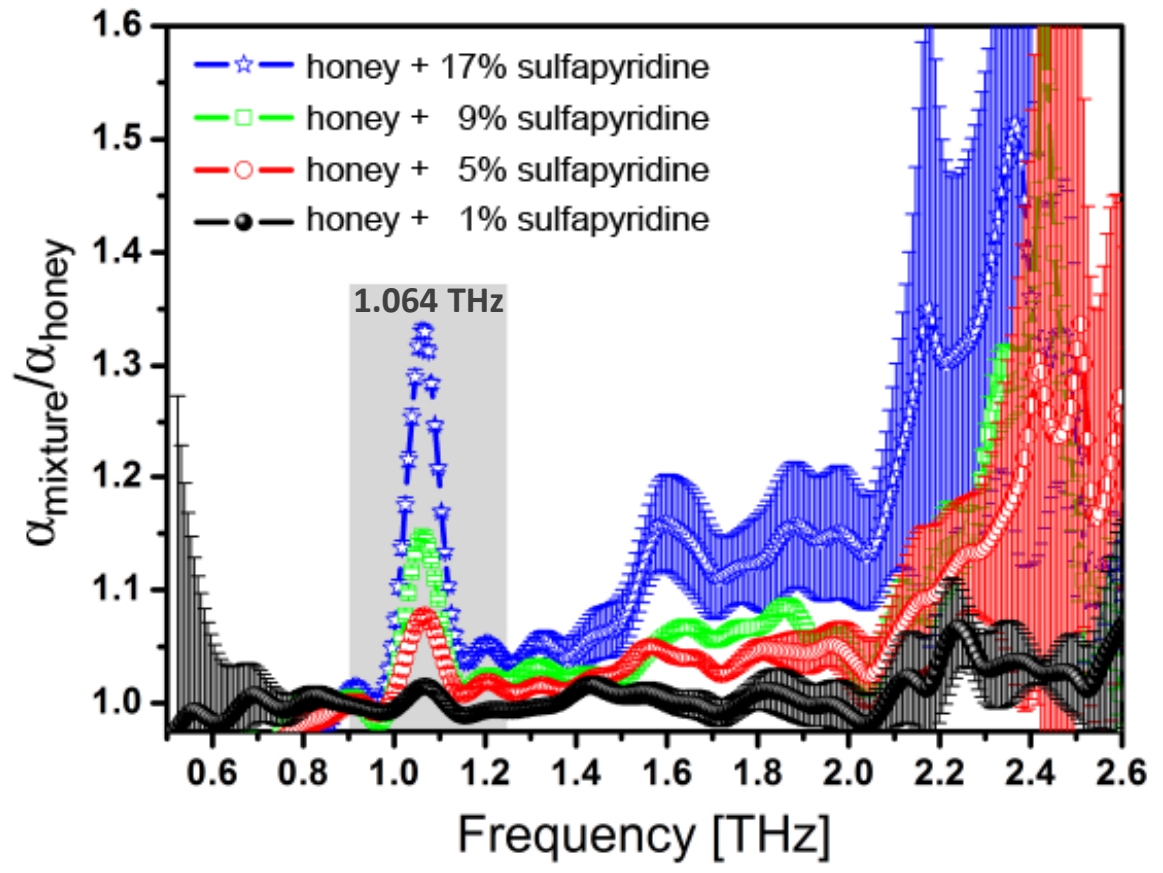
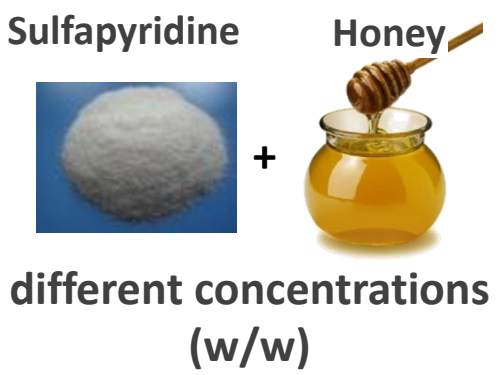
$$\alpha_{mixture} \propto \frac{A_{mixture=honey+sulfapyridine}}{A_{THz.ref}}$$

# Sulfapyridine in honey

## SAMPLE HOLDER (liquids)



## Mixture:



Detection of Sulfapyridine in honey at relatively low concentrations (1% w/w)



# Sulfapyridine & Sulfathiazole in honey

Massaouti et al. J. Appl. Spectr. (2013)

## Multiple residues in honey

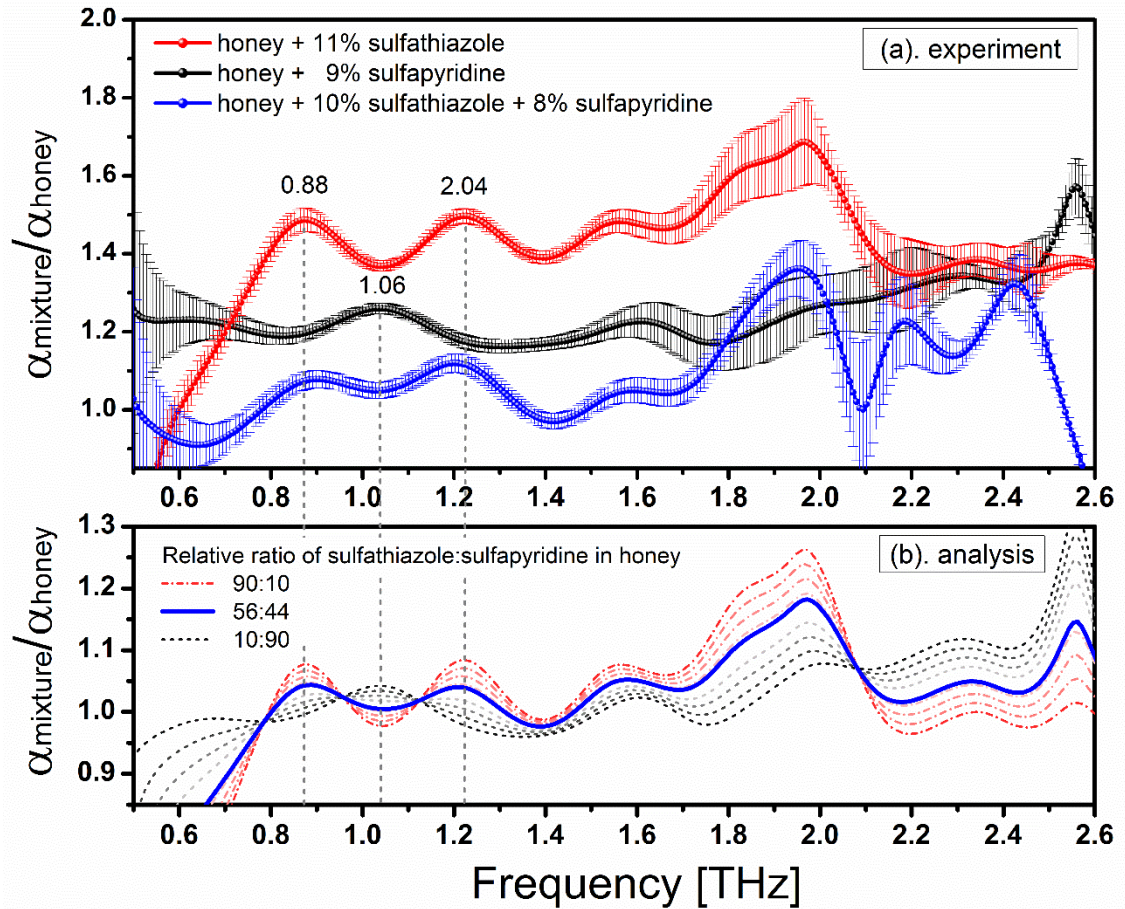
Mixture:

Sulfapyridine (9%)  
and  
Sulfathiazole (11%)



$$\alpha_{\text{binary mixture}} / \alpha_{\text{honey}} = \sum_i B_i \cdot \alpha_i / \alpha_{\text{honey}}$$

$i = \text{sulfapyridine, sulfathiazole}$



Potential of THz-TDS to be used in the near future as a fast, real-time technique for detecting and discriminating multi-residues strictly related to food safety issues.



<http://www.iesl.forth.gr/>



LASERLAB-EUROPE



## Acknowledgments

UNIS - THz group <http://unis.iesl.forth.gr/>

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Dr. A. Gorodetsky

M. Loulakis

T. Koulouklidis

C. Daskalaki



UNIS group