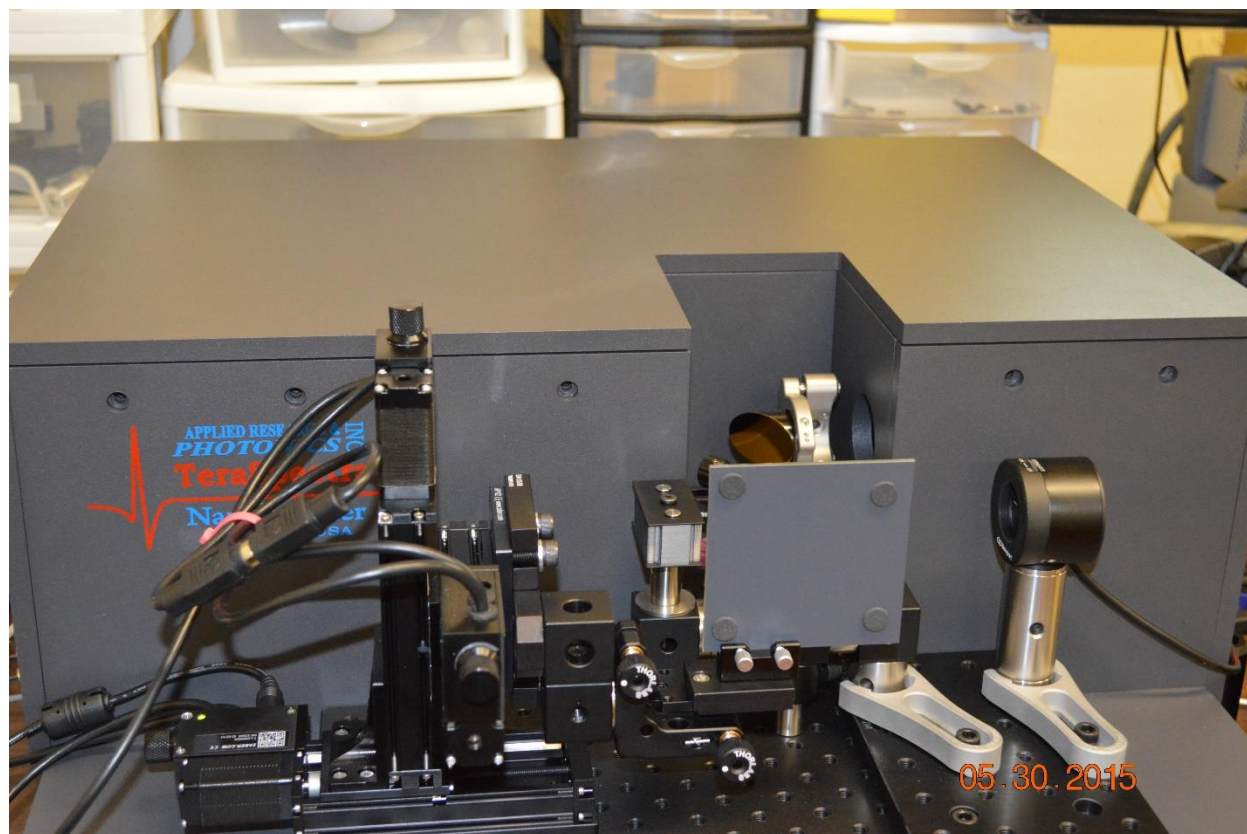# A wideband spectrometer to fill the Terahertz Gap!

TeraSpecta with integrated nanoscanner: A powerful new tool for chemical analysis

ARP's TeraSpectra is a turn key spectrometer based on **Terahertz time-domain spectroscopy (THz-TDS)**. TeraSpectra uses a proprietary EO dendrimer source that generates stable terahertz radiation from 0 – 30 THz at room temperature.

The front-end allows the user to set the time window to capture molecular events that happen at different rates. The result is a unique analytical tool that can probe samples across the entire Terahertz gap.

TeraSpectra can identify and quantify pure or component chemical species down to femtomolar or parts-per-trillion levels in solid materials, liquids or gases. The instrument can recognize the signature of molecules that are opaque to radiation from other parts of the spectrum or lack chromophores. It can be used to discern fine molecular structure such as atomic substitutions as small as a single hydrogen or multi-centered chirality. By adjusting the time window, THz spectra can capture the kinetics of binding or dissociation. This can range from the formation of intermediates to the binding of ligands to molecules, large complexes, colloids, particles or even solid surfaces. In addition, a scanning reflectometer can measure the kinetics of and the depth to which compounds absorb into solid matrices such as skin or other porous surfaces.

What is time- domain terahertz spectroscopy?

THz-TDS is a spectroscopic technique in which measurements are conducted in the time-domain on a scale of femto-seconds to a few tens of pico-seconds. An appropriate Fourier transform is applied to a measured terahertz pulse, which generates the terahertz spectrum. The generation and detection scheme is sensitive to the sample material's effect on both the amplitude and the phase of the terahertz radiation. In this respect, the technique provides much more information than conventional Fourier-transform infrared spectroscopy or Raman spectroscopy, which is only sensitive to the amplitude. Terahertz wavelengths correspond to room-temperature; as such the technique allows probing many molecular systems in their native state (e.g., biological systems) without ionizing radiation.

Principle of THz Spectroscopy

When THz radiation interacts with molecules, it may stimulate many resonances such as molecular vibrations, phonons and/or other resonances in the system, resulting in the THz photons being affected by a specific interaction or event. The change in energy and/or frequency yields information about the molecular nature of the interaction. Infrared and Raman spectroscopy, for example, yield similar information but are not capable of detecting as many resonant states as can be detected with THz because **terahertz photons are sensitive to the vibrational states of the entire molecule,** not just a bond or charge state. Molecular vibrations can range from the simple coupled motion of the two atoms

in a diatomic molecule to the much more complex motion of each atom in a large polyfunctional molecule. In general, each atom will have 6 degrees of freedom (with restrictions in some cases); thus a molecule composed of N atoms will have $6N$ vibrational states. Such structures are easily probed by terahertz spectrum.

THz-TDS has several distinct advantages over other forms of spectroscopy. Materials have unique spectral fingerprints in the terahertz range, which means that terahertz radiation can be used to identify them. Examples which have been demonstrated include polymeric explosives, polymorphic forms of many compounds used as Active Pharmaceutical Ingredients (APIs) in commercial medications and chiral compounds with single or multiple chiral centers. Many materials are transparent to THz radiation that is opaque to other wavelengths. Because of this, samples can be seen and measured through visually opaque intervening layers, such as packaging or fabrics. Spectroscopic or image analysis of samples at or below opaque or buried interfaces and defects can be found and precisely characterized or imaged. Finally, unlike X-Rays or UV, measurements made using THz radiation are non-contact and safe for biological tissues because they are non-ionizing

Product Description

ARP's TeraSpectra is the first low cost benchtop THz-TDS spectrometer to analyze samples across the entire "terahertz gap", from 100GHz to 30 THz at room temperature. The product's unique capabilities arise from the patented source and detector technologies (EO dendrimer) employed in the design. ARP uses a dendrimer-based high power source pumped with two diode lasers where the beam is split into two arms: one arm remains stationary while the other arm scans the stationary beam that produces an interferogram, characteristic of the specimen-THz interaction. Signals from 100 GHz to 30 THz can be generated and detected by this method with an average power of >5 mW.

TeraSpectra can be used to measure unique compositional and chemical features in samples not able to be measured with other spectroscopic techniques or other terahertz instruments not using EO technology.

As a high sensitivity device it can be used to identify and monitor the effect of binding of one molecule to another, or their dissociation. Unlike Raman or IR spectroscopy, terahertz energy can penetrate to probe at a deeper level. Molecular

signature recognition and trace analysis may be conducted at concentrations as low as femto-molar or parts per trillion. Other analyses such as conjugation and catalysis can also be done on a molecular level. Since the time window of the measurements can be varied, fast or slow events on the molecular level can be measured. Slower events such as protein-protein interactions, enzyme reactions, or any biological process can be identified and studied for THz spectral responses due to chemical, temperature or other environmental stimuli and monitored with high precision.

TeraSpectra Specifications

Parameter	TeraSpectra[1]
Time resolution	<100 Femto-seconds
Time span	Up to 100 Pico-seconds
Frequency Range	0.1 to ~30 terahertz
Technology	Next gen. EO dendrimer
Source power	>5 milliwatts
Sensitivity	~ 200 FemtoMol
Operation condition	Ambient
Mode	Transmission/Reflection

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[1] Specification may change

Product Features

- TeraSpectra is cost-effective with higher performance because of its next generation dendrimer technology.

- A high power source enables probing of a wide variety of specimens thus expanding the scope of the spectrometer.

- Both transmission and reflection (optional) measurements

- Solid, liquid and gaseous specimens

- High Signal to Noise Ratio.

- Label-free characterization.

- Room temperature operation.

- Stabilized, ~1" beam diameter for uniform exposure. Beam size may be focused to suit other requirements (optional)

- Temperature and Environment control chamber (option).

- Collaborative investigations available for demonstration of new applications.

TeraSpectra Performance Example
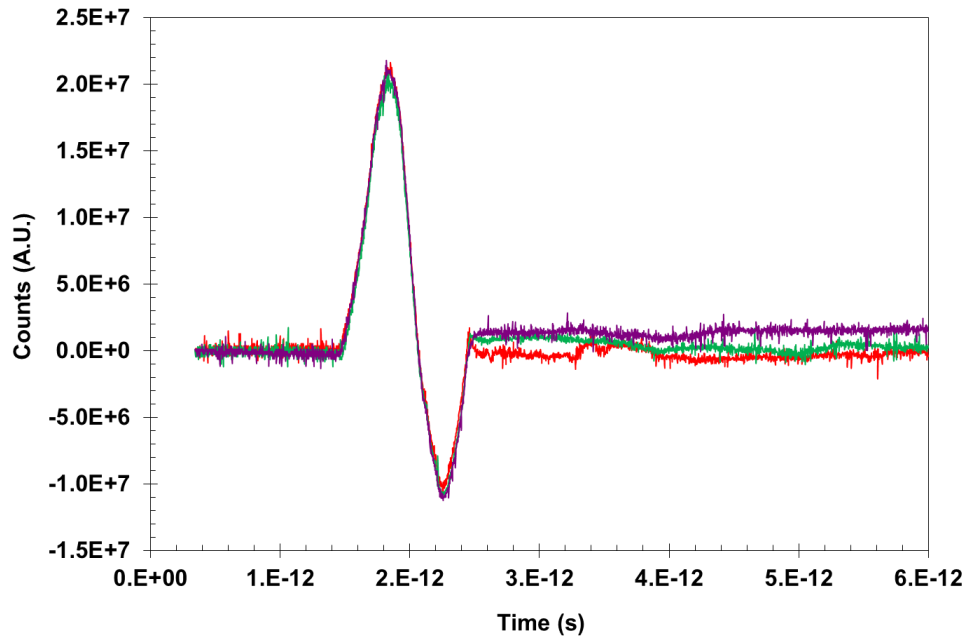
Fig. 2. Typical time-domain signal (pulse, or interferogram) exhibits sub-pico second full width at half maximum (FWHM).
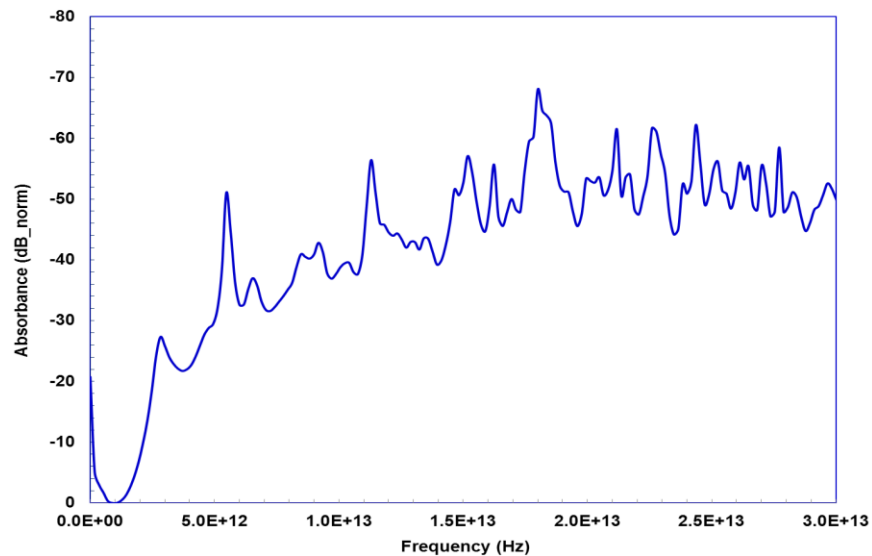

Fig. 3. Frequency-domain spectrum spans over a wide frequency range.

Validation of Data

Here a comparison is produced of terahertz spectra of water with those from the NIST [1]. The **complete spectrum** is given in the white paper [2] and compared with other work on water/vapor.
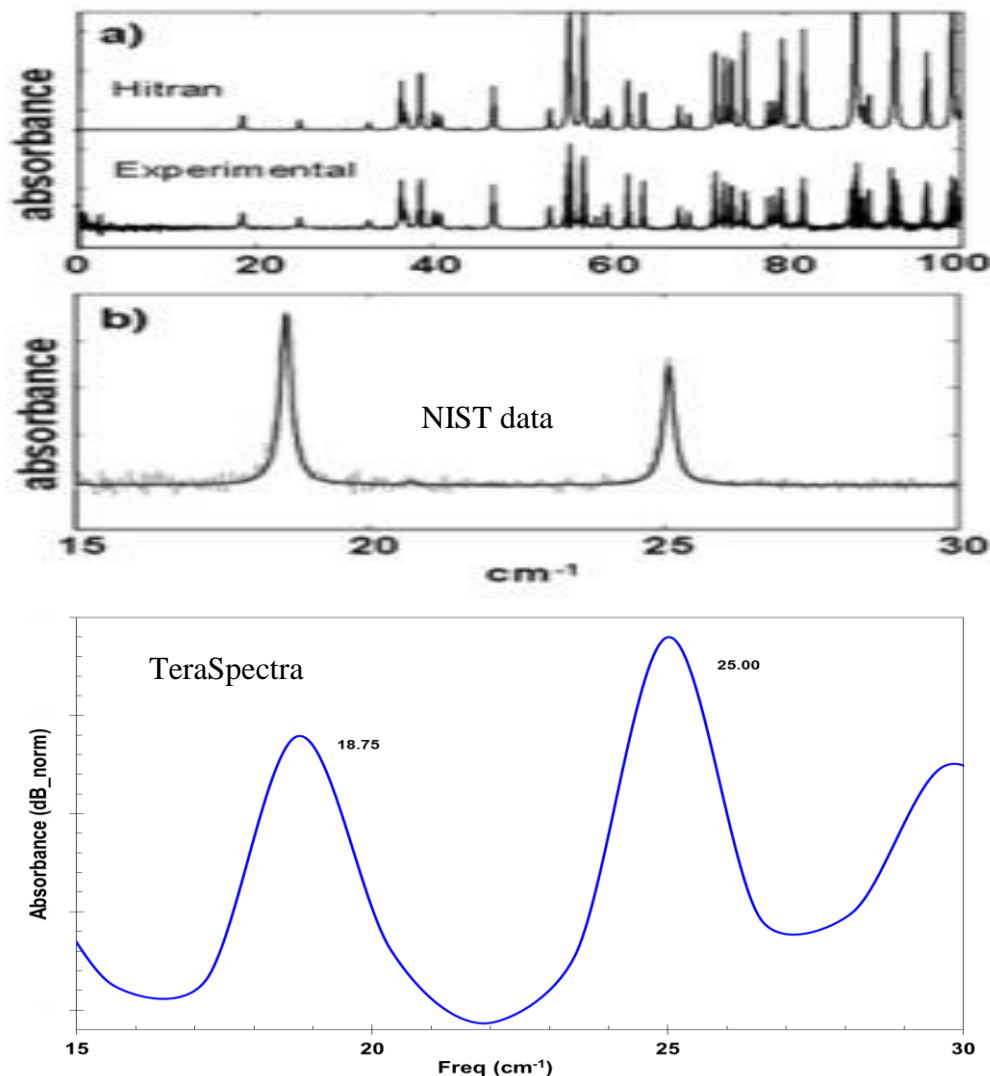

Fig. 4. Top: Water vapor absorption spectrum obtained using the THz spectrometer compared to that calculated using the HITRAN database by the NIST. An expanded portion in the panel (b) containing pressure broadened water lines from NIST. Bottom: Expanded view of vapor absorption lines obtained from ARP's TeraSpectra (see ref). Low frequency peaks match well with those reported by the NIST [1].

[1] http://physics.nist.gov/Divisions/Div844/facilities/thz/Images/Fig2.png

[2] Ref: http://arphotonics.net/WaterVaporComparison1.pdf

Operation Details

TeraSpectra is a turn-key spectrometer equipped with a user-friendly front-end and also a sophisticated analysis package via third party. It requires minimal sample preparation and can measure samples in solid, liquid and gaseous forms. A host of samples can be measured by dissolving in to a suitable solvent (both aqueous and organic) and then dispensing a small amount of the solution on a glass slide. Once the solvent is dried, the remaining residue can be mounted in the spectrometer using a XYZ-stage (supplied), see Fig. 14. For liquid samples a small path-length cuvette is used (also supplied).
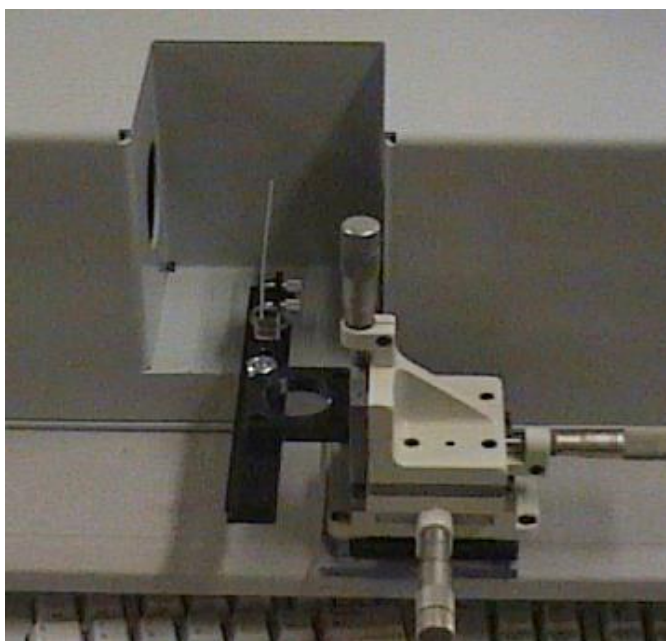
Fig. 5.   Sample (spot) on a glass slide mounted on a XYZ-stage placed in the beam path.

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Data Analysis

TeraSpectra data is fully compatible for a host of analysis functions provided by the accompanying bundled software. Following is a summary of functions available from the package via drop-down menu:

Fourier Spectral Analysis

Fourier Spectrum
Fourier Spectrum with Data Window
Fourier Spectra with Data Window Comparison
Fourier Spectra of Segmented Data
Fourier Multitaper Spectra
Fourier Spectrum of Unevenly Sampled Data

AR, MA, and ARMA Spectral Analysis

AR (AutoRegressive) Spectrum
AR Spectrum with Order Exploration
AR Spectrum with Algorithm Comparison
MA (Moving Average) Spectrum
ARMA (AutoRegressive Moving Average) Spectrum

Prony, Minimum Variance, and EigenAnalysis Spectral Analysis

Prony Spectrum
Minimum Variance Spectrum
EigenAnalysis Spectrum

Time-Frequency Spectral Analysis

Short Time Fourier Transform Spectrum
Continuous Wavelet Spectrum (3D Surface)
Continuous Wavelet Spectrum (2D Contour)
Continuous Wavelet Spectrum Frequency Range
Continuous Wavelet Spectrum Time Range

Denoising/Smoothing

Fourier Smoothing and Denoising
Eigendecomposition Smoothing and Denoising
Wavelet Smoothing and Denoising
Savitzky-Golay Smoothing Filter

Interpolation/Smoothing

Fourier Interpolation
Spline Estimation
Non-Parametric Estimation

Software features (cont'd)

Fourier Upsampling

FIltering and Reconstruction

Fourier Filtering and Reconstruction
Eigendecomposition Filtering and Reconstruction
Wavelet Filtering and Reconstruction

Prediction
  Parametric Interpolation and Prediction
  AR Linear Prediction

IRF Deconvolution
  Deconvolve Gaussian Response Function
  Deconvolve Exponential Response Function

Informational
  Autocorrelation
  Fractal Dimension
  Compare Imported Reference

The following advanced processing procedures are available via drop-down menu:

Fourier Smoothing and Denoising is a specialized Fourier filtration procedure that sets either a frequency threshold for low pass frequency-domain filtration, or a signal threshold for zeroing all spectral elements below a given dB (normalized) value. The time domain data are reconstructed using the inverse FFT.

Eigen decomposition Smoothing and Denoising filtration occurs by zeroing those Eigen modes in an Eigen decomposition of the data matrix that lie beyond a specified signal-noise threshold. By using higher order decomposition, it is often possible to remove nearly all of the noise within a signal.

Wavelet Smoothing and Denoising is similar to the Fourier procedure except that the thresholding is done in the time-frequency domain. The analyzing wavelet is fully adjustable, although the size and scales are fixed for reconstruction and the format is limited to an adjustable dB contour. Although frequency thresholding is offered, the main functionality comes from setting a wavelet spectrum threshold below which all values are zeroed prior to a CWT reconstruction. This option is effective in smoothing and denoising non-stationary data.

Fourier Filtering and Reconstruction option is an extensive Fourier domain filtering and component isolation procedure. It is possible to set lower and upper frequency thresholds as well as lower and upper spectrum thresholds. A given portion of the spectrum can be included or excluded by graphical sectioning. Individual frequencies can also be toggled on and off. Data windows are available, primarily to minimize spectral leakage so that very low power components can be isolated and reconstructed. When some frequencies are zeroed within an exact n non-windowed FFT, and the reconstructed data is again processed by an exact n non-windowed FFT, there will be true brickwall transitions at the zeroed frequencies.

Eigendecomposition Filtering and Reconstruction offers full eigenmode filtering and reconstruction. This allows components to be isolated by signal strength. In addition to reconstructing the data, the reconstruction can optionally consist of the eigenvectors, the principal components, the data components, FFTs of the data components, an FFT of the data, AR spectra

of the components, or an AR spectrum of the data. Two eigenmodes are required to capture an oscillation. For this reason eigenmodes often appear in pairs. Unlike the FFT, eigendecomposition is non-parametric. A non-sinusoidal anharmonic oscillation is captured as easily as a sinusoidal harmonic.

Wavelet Filtering and Reconstruction offers the means to reconstruct signals from spectral components that have been isolated in the time-frequency domain. Time, frequency, or spectral ranges can be set numerically or regions can be included or excluded graphically. The analyzing wavelet is fully adjustable, but the other elements are fixed by the reconstruction requirement. When a signal's spectral content varies across time, this option can readily isolate components that appear and disappear. Components that undergo changes in amplitude and frequency with time can also be characterized.

Fourier Interpolation is similar to the **Fourier Filtering and Reconstruction** option except that the reconstruction is computed directly from the amplitude, frequency, and phase of the sine components rather than by an inverse FFT. This offers a reconstruction where the data count and limits are variable. This option thus offers interpolation based upon the frequency spectrum. This means that any size reconstruction will generate this same spectrum. When the data count is increased, the frequencies beyond the original Nyquist can be zeroed using a low pass filter option. In addition to reconstructing the basic data, this option also makes it possible to reconstruct the first, second, third, or fourth derivatives.

Fourier Upsampling uses the traditional zero-insertion approach to interpolate data. This procedure is limited to integer upsampling ratios and all frequencies beyond the original Nyquist will always be zeroed. Since this procedure uses the inverse FFT for the reconstruction, it is very fast.

Parametric Interpolation and Prediction is a powerful composite algorithm that generates a parametric (sinusoids or damped sinusoids) model of the signal. The algorithm has three stages. In the first stage, a procedure is used to estimate the frequencies and component count. There are five algorithms for equally spaced data, and three ranges of the Lomb algorithm for data that are not uniformly sampled. The best algorithms use SVD for removing the influence of observation noise. In the second stage a linear fit is made to determine the amplitudes, phases, and damping factors. These are the starting estimates for the third stage, the non-linear optimization that fully refines the parametric estimates. To facilitate prediction tests, it is possible to specify that only a portion of the data set be processed. Subsequent data can then be compared with the predicted points. The generated data bounds and count are fully variable.

Deconvolve Gaussian Response Function manages the instance where a signal is smeared by a Gaussian response function. The deconvolution seeks to recover the true signal that would have been measured using an ideal sensing system.

Deconvolve Exponential Response Function is for instances where a signal is smeared by a first order or exponential response function. This is always a one-sided deconvolution that seeks to recover the true signal absent the delay of the measurement system.
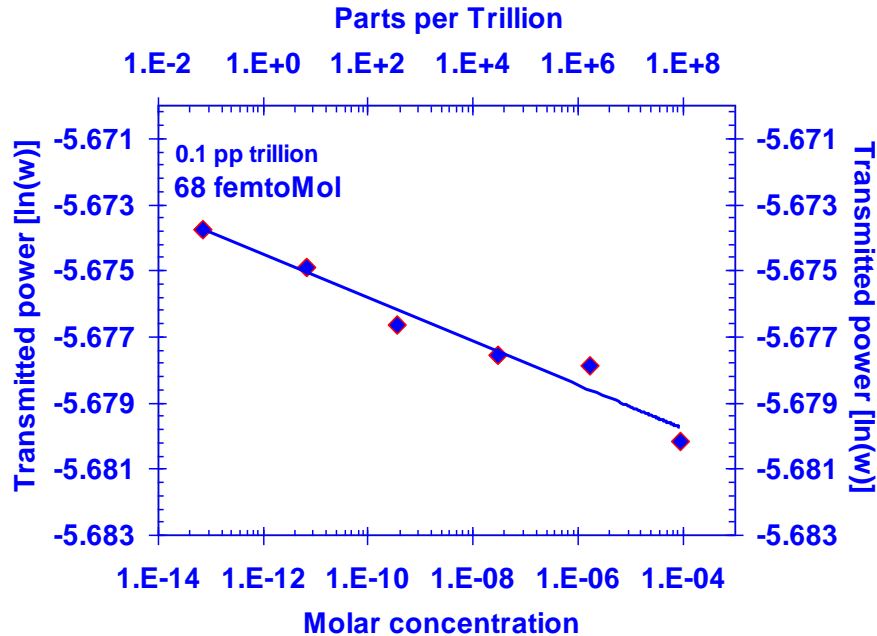
Application Examples

Fig. 6. Quantitation of an organic compound (Ceraphyl) at parts per trillion (or femtomolar) concentration from an organic solution (methanol).
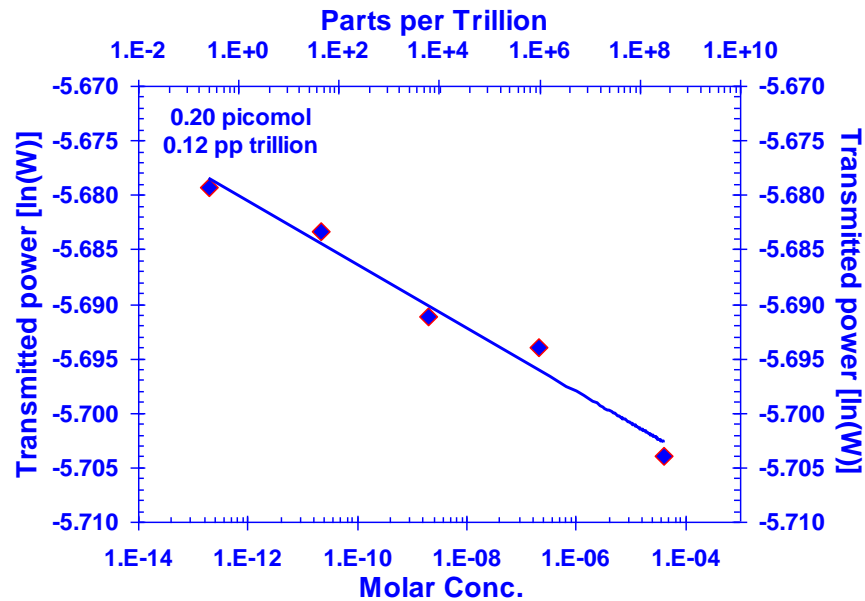

Fig. 7. Detecting at parts per trillion of an inorganic salt (Cr³ Acetate Hydroxide) from aqueous solution.
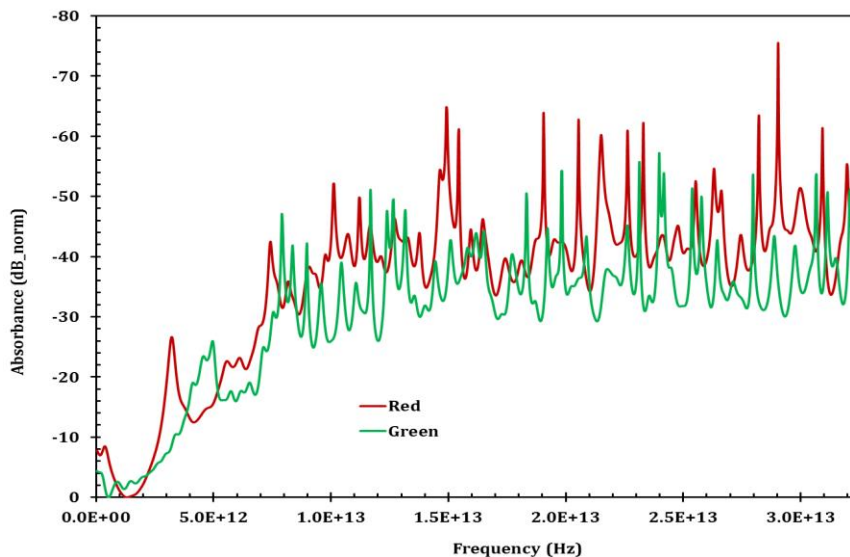
Fig. 8.   Spectra of emulsions used in beverage flavoring to allow instant estimation of product stability. Represents stable vs. unstable samples of the same product.
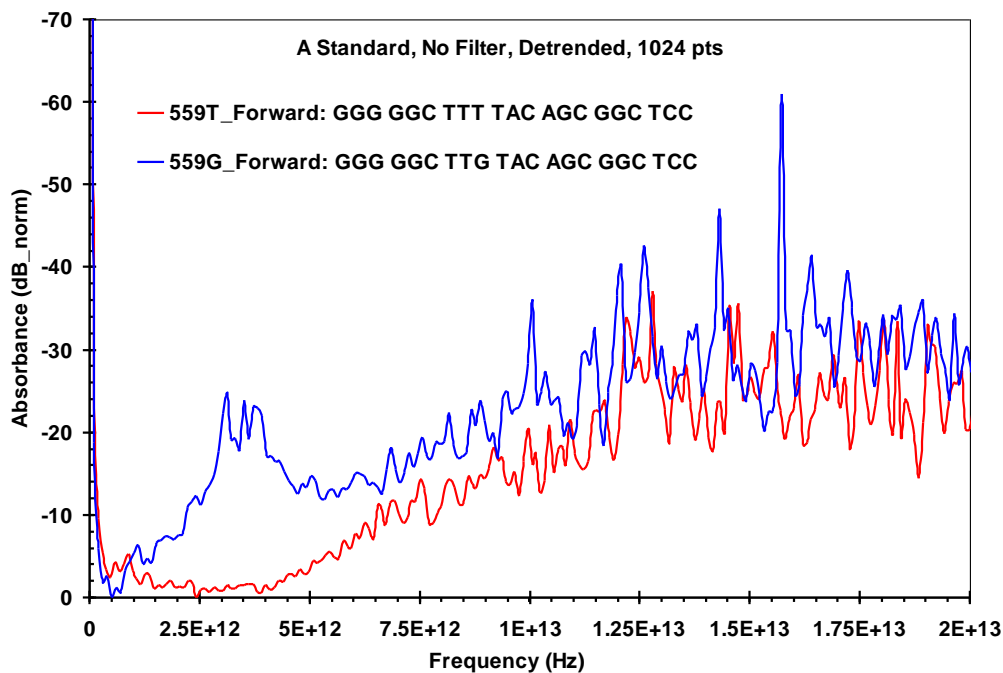

Fig. 9.   Two 21-mer oligonucleotides '559T' and '559G' of FCGR3A gene with and without SNP (559T>G) were synthesized at the Penn State College of Medicine Synthesis Lab using a POLYGEN synthesizer. The absorbance spectra exhibit clear difference when a Thymine is substituted by Guanine.
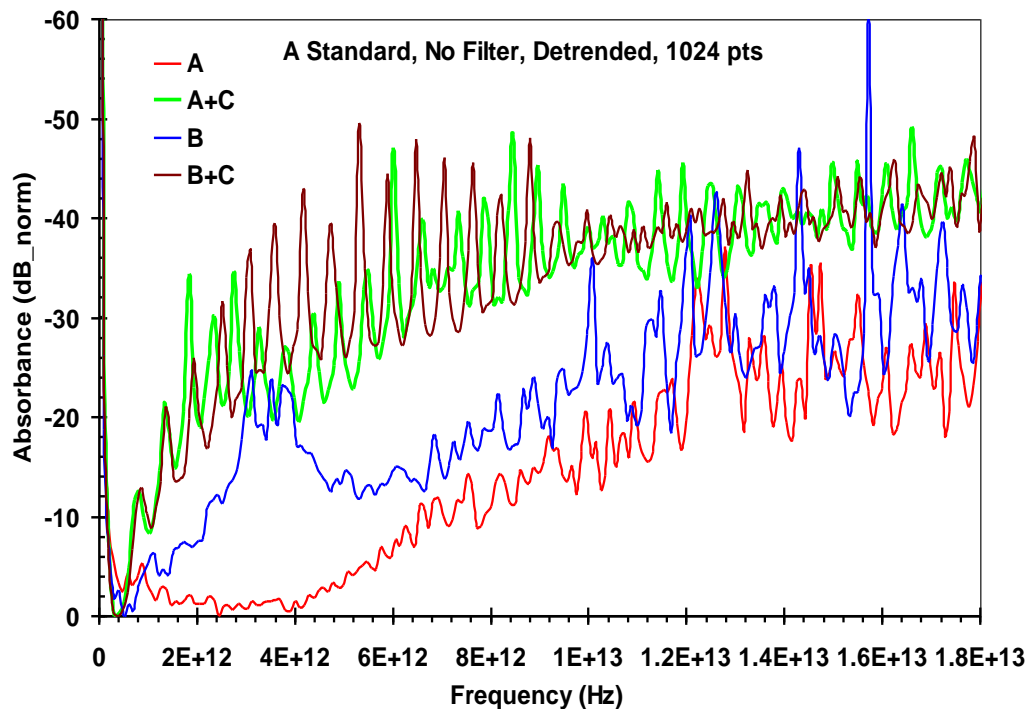
Fig. 10. DNA hybridization state -Absorbance spectra of single-stranded (A & B) and double-stranded (A+C & B+C) (hybridized) DNA. Characteristic peaks allow distinguishing between the hybridization states without labeling. Samples complement of Penn State College of Medicine, Hershey, PA.
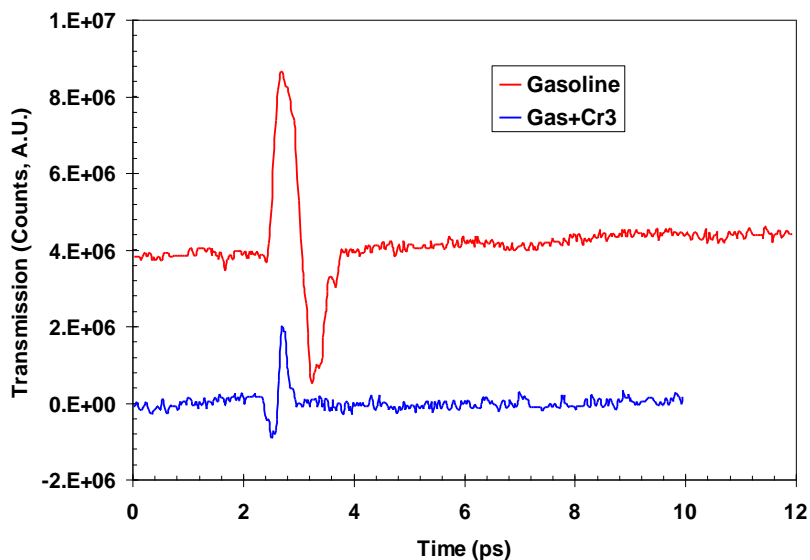
Fig. 11. Normalized time-resolved spectra of gasoline (red) and Cr (III) Acetate Hydroxide $[(CH_3CO_2)_7 Cr_3 (OH)_2]$ solution in gasoline at 1.91 mg/ml (blue). Presence of salt in gasoline reduces the transmission of THz power through the sample.
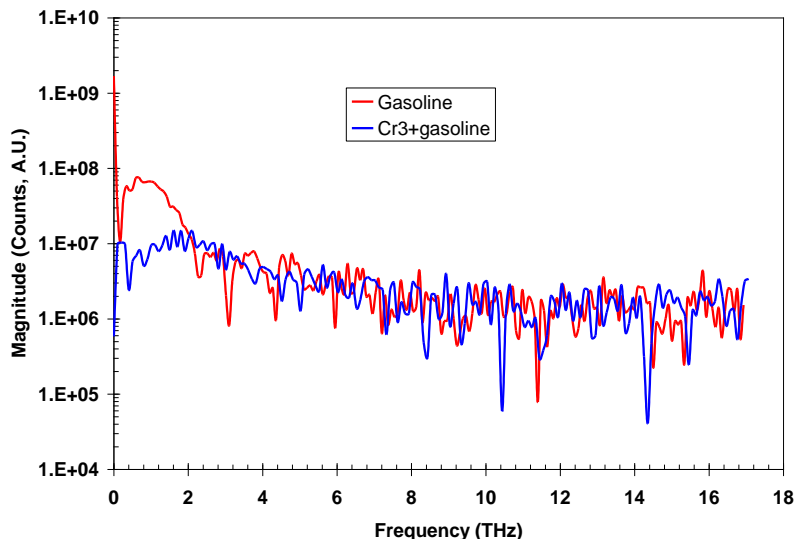
Fig. 12. **Fourier spectra of gasoline (red) and 1.91 mg/ml CrAH solution (blue) corresponding to the time-resolved spectra of Fig. 1. The spectra are clearly different allowing differentiating between the two samples. (Cuvette effect, if any, was not subtracted).**
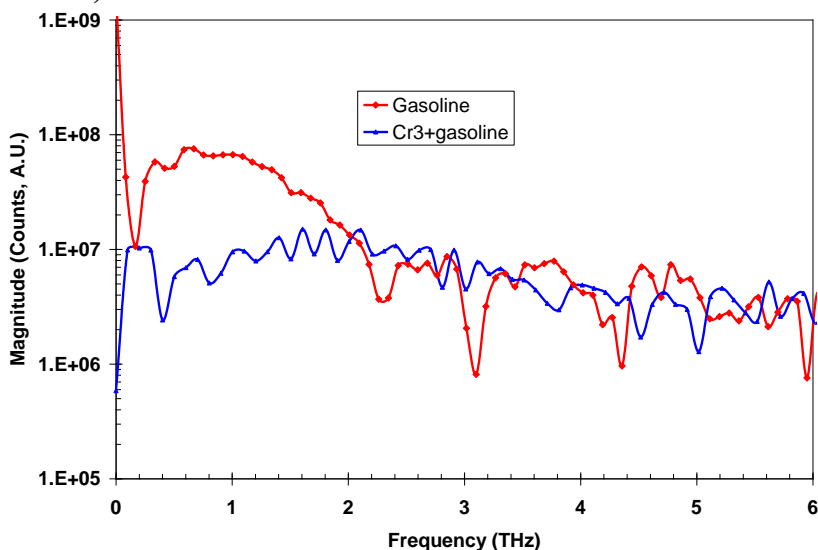
Fig. 13. **Close-up of spectra in Fig. 11. An interesting observation is that at low frequencies below ~2.25 THz gasoline (red) exhibit higher transmission than CrAH solution (blue). However, at higher frequencies (above ~2.25 THz) gasoline exhibits a few absorption peaks that are not present in the CrAH. Thus the frequency dependent behavior of the two specimens reveals some interesting molecular interaction between the CrAH and gasoline that can not be fully understood from the present data.**

Analysis Examples
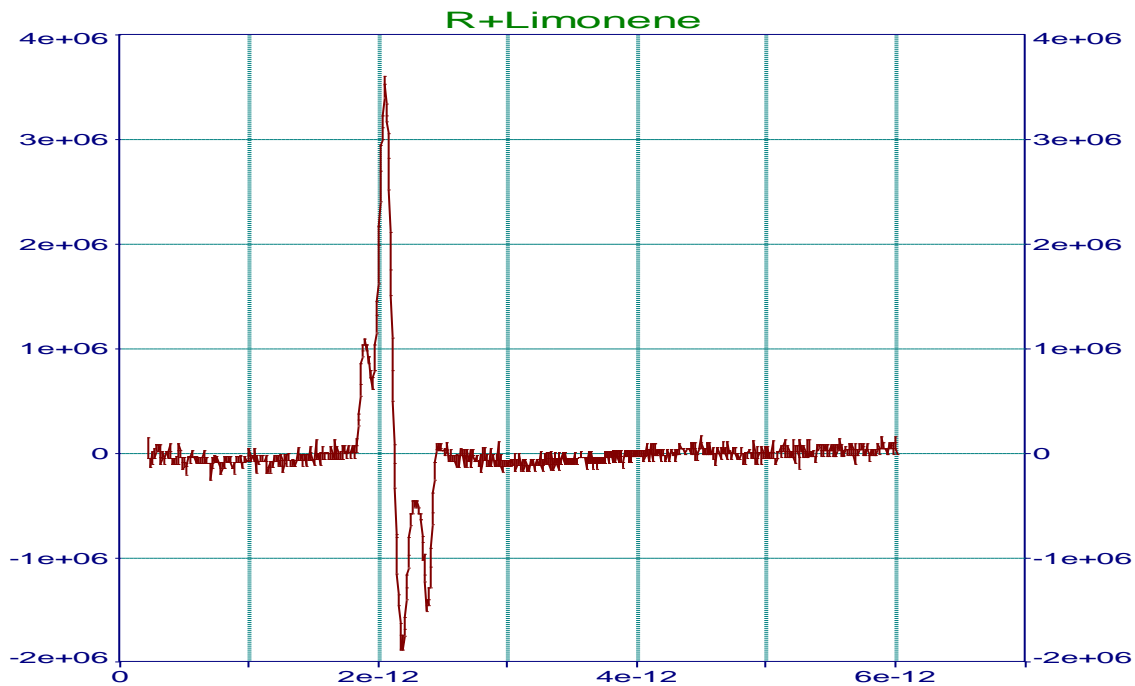
Fig. 14. Terahertz signal obtained for R+ Limonene without dilution. ~30μL sample was placed on a glass slide for measurement.
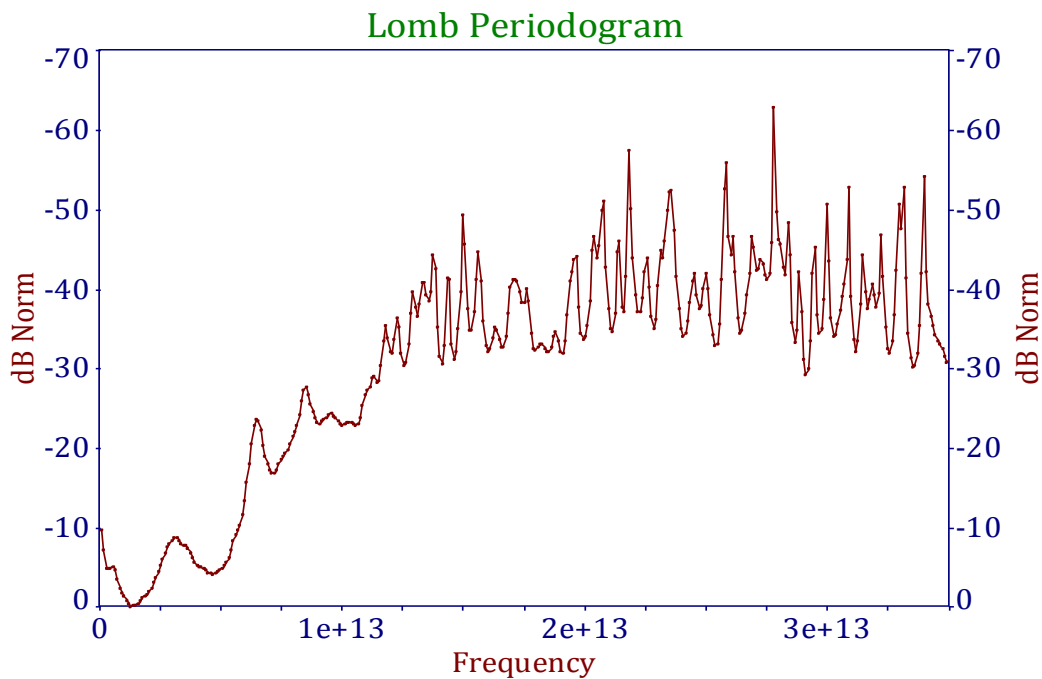

Fig. 15. Frequency domain spectrum of R+ Limonene obtained from Fig. 14.
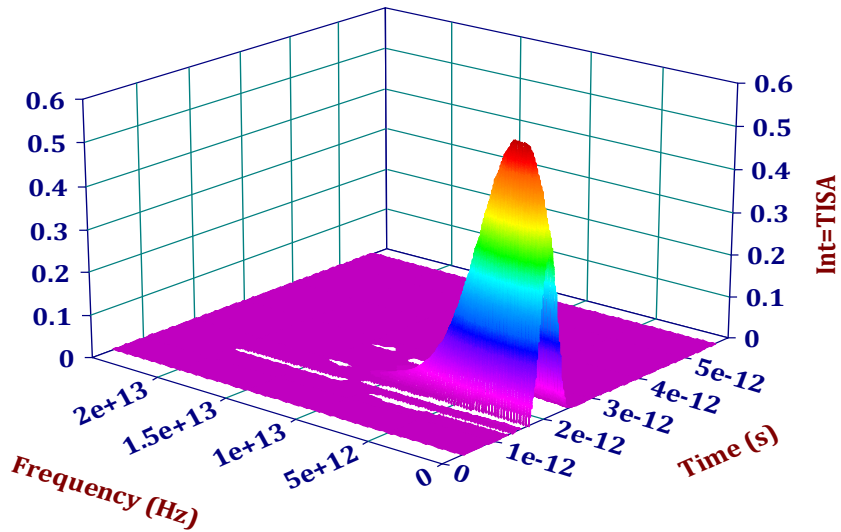
Fig. 16. Short-Time Fourier transform spectrum of R+ Limonene give frequency spectrum but also preserves time information.
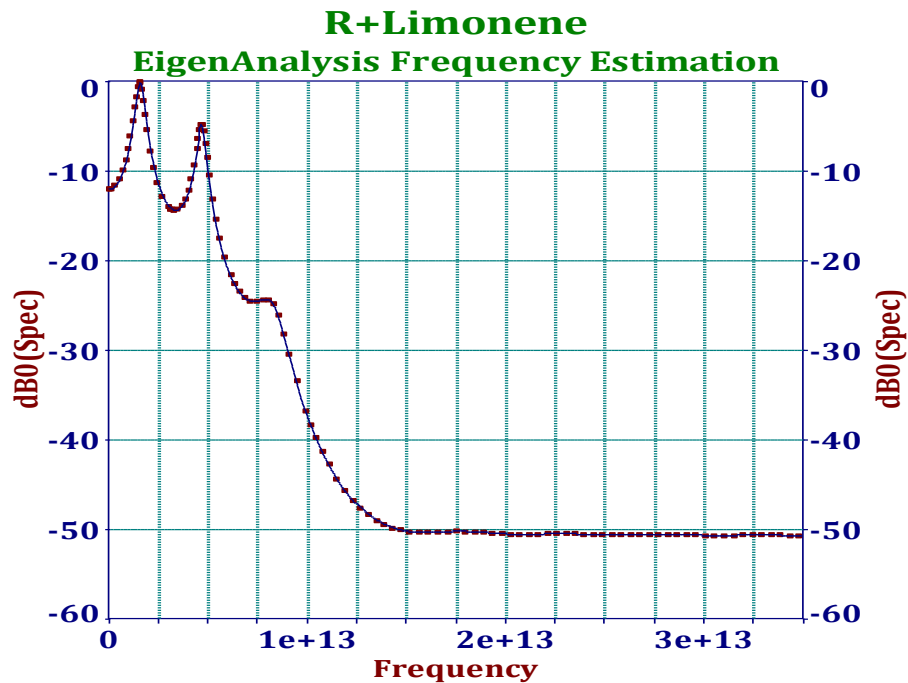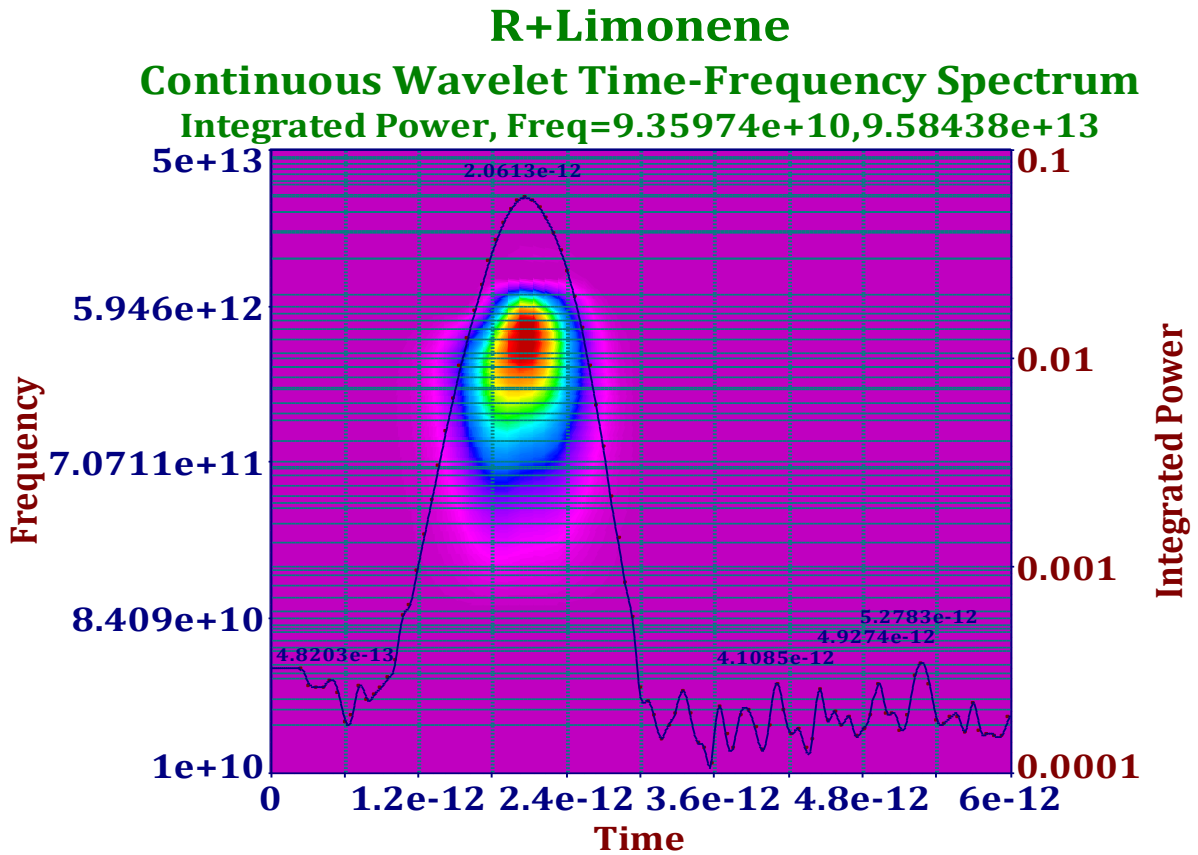

Fig. 17. Eigen frequency analysis of the spectrum.

R+Limonene
Continuous Wavelet Time-Frequency Spectrum
Integrated Power, Freq=9.35974e+10,9.58438e+13

Fig. 18. 2D wavelet transform
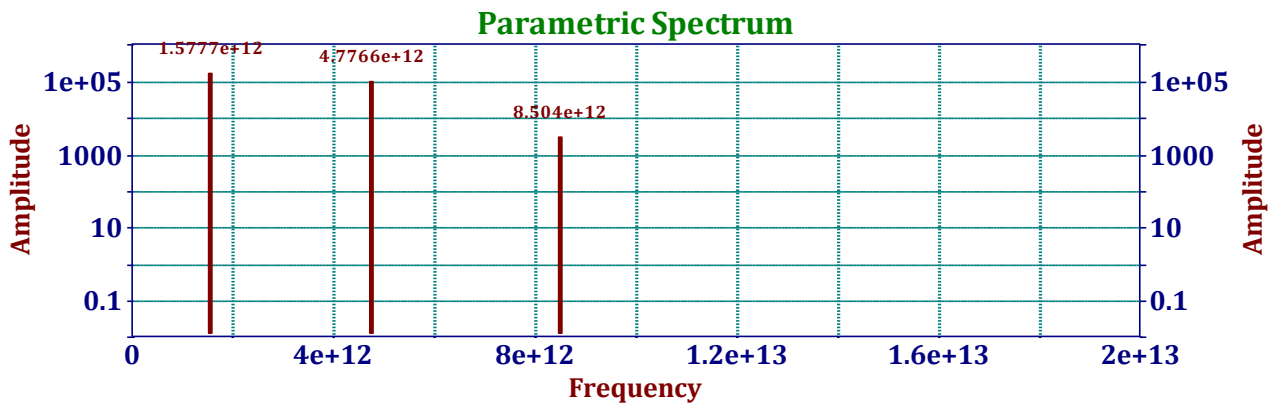
Parametric Spectrum

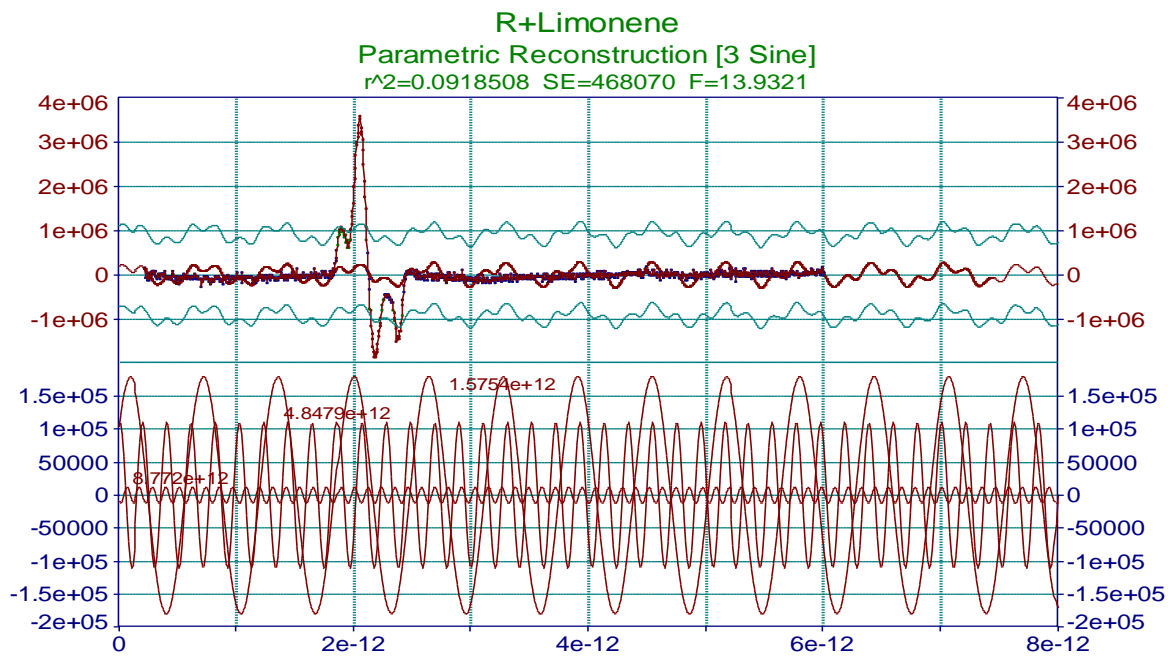
Fig. 19. Parametric spectrum analysis

Fig. 20. Decomposition of the time-domain signal in to 3 sine functions.