



Segmented Chirped Pulse Fourier Transform (CP-FT) Millimeter Spectroscopy: *Identification of Volatiles by Pure Rotation*

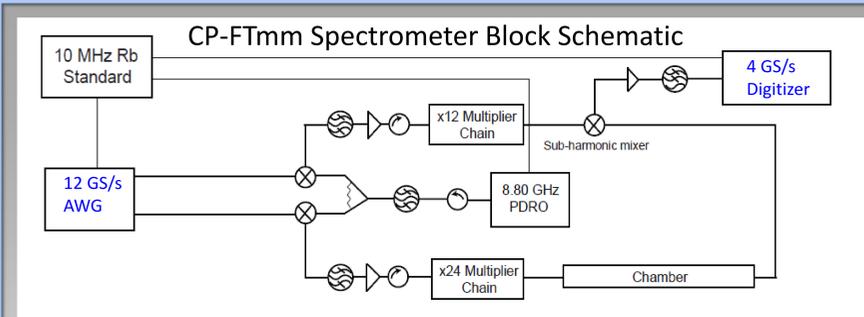
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Introduction

Ever increasing environmental regulations require new methods for trace chemical detections in complex matrixes. Millimeter spectroscopy offers a high resolution measurement that is geometry and mass specific for small volatile molecules with a dipole moment.

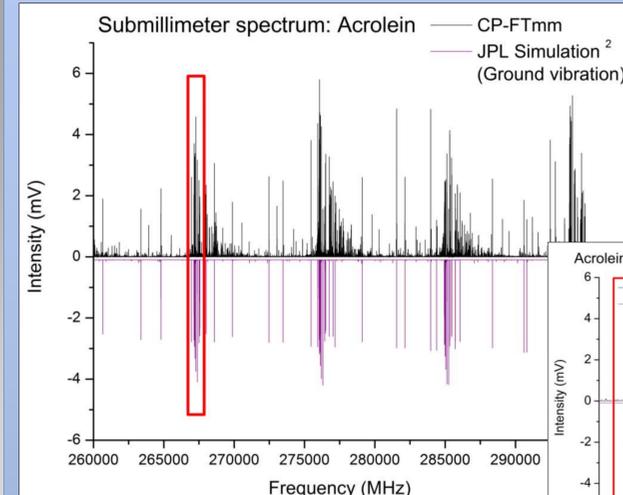
Chirped Pulse Fourier Transform sMillimeter (CP-FTmm) spectroscopy is a background-free emission technique that offers advantages over absorption measurements. CP-FT maximizes sensitivity by spreading all of the available excitation pulse power across a broad band sweep rather than attenuating the power in a stepped scan in order to avoid molecular saturation limits.¹ This yields highly accurate quantitative abundance measurements in short time periods.

In a **segmented** experiment, several excitation and emission events at narrow bandwidths are combined to construct the fullband spectrum. Without loss in sensitivity, segmenting enables low instantaneous bandwidth requirements accompanied by a cost reduction and better leveled response curve than fullband Chirped Pulse.

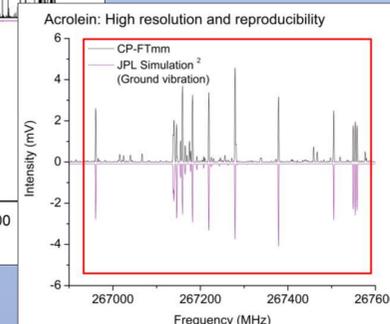


- An Arbitrary Waveform Generator (AWG) generates the excitation pulse at low frequency and bandwidth (2-4 GHz).
- A 24X multiplier chain multiplies the pulse to millimeter (260 – 290 GHz).
- The pulse travels through a single pass 0.75m sample cell.
- Emission is digitized at low frequency (720 – 1440 MHz) via heterodyne detection scheme
- Frequency accuracy is accomplished by reference to a Rubidium clock

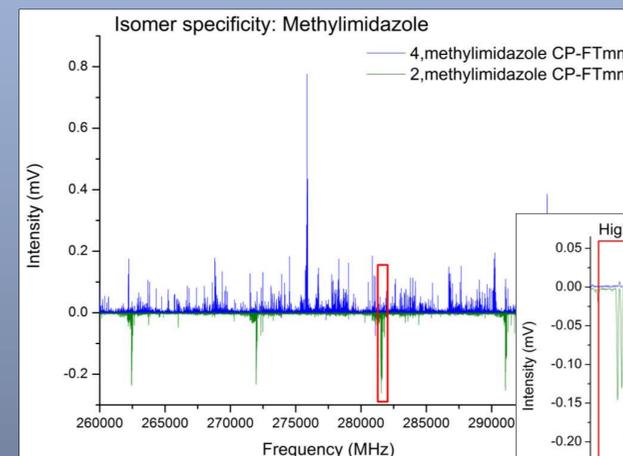
Liquid Injection: Acrolein and JPL catalogue²



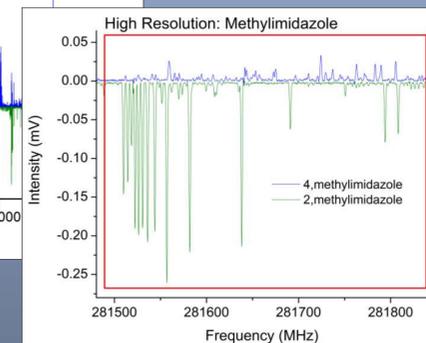
A toxic combustion byproduct, acrolein has a no significant risk limit (NSRL) at 3ppb over 24 hours.³ There is no method in place to measure at ppt in order to establish a lower zero detection limit.



Solid Headspace: Methylimidazole



A carcinogenic byproduct of caramel colored dyes, methylimidazole has a food product exposure limit of 16µg per day for the 4-methylimidazole isomer.⁴



Conclusion

The high resolution, sensitivity, and specificity of sub millimeter spectroscopy make it an ideal method for volatile mixture analysis.

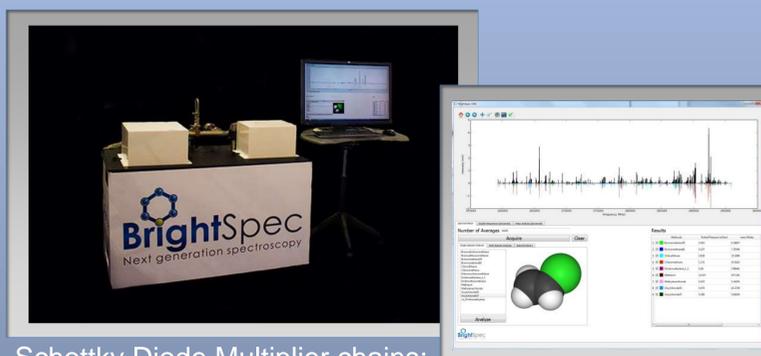
The CP-FTmm spectrometer accomplishes a broadband (30 GHz), fast (approx 1 sec acquisitions above), low frequency detection method for measurement by pure rotational spectroscopy.

Segmented CP-FTmm enables a practical solution. It can be designed for calibration-free standalone operation without any moving parts or complicated optics.

Sample introduction can be accomplished by conventional techniques such as liquid injection, headspace sampling, chromatography, or pre-concentration.

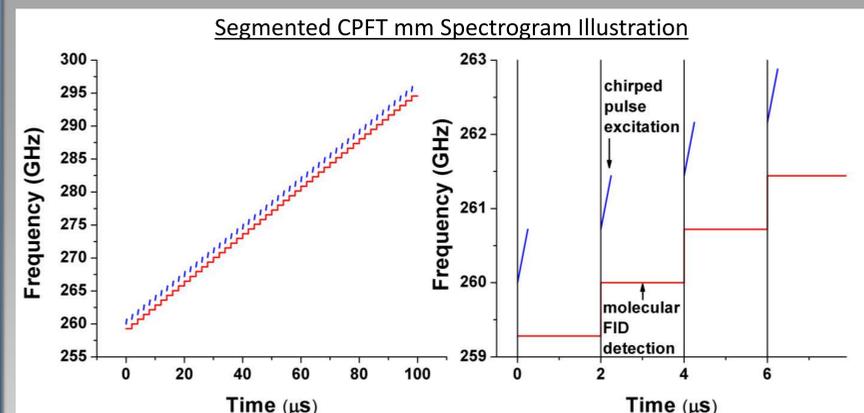


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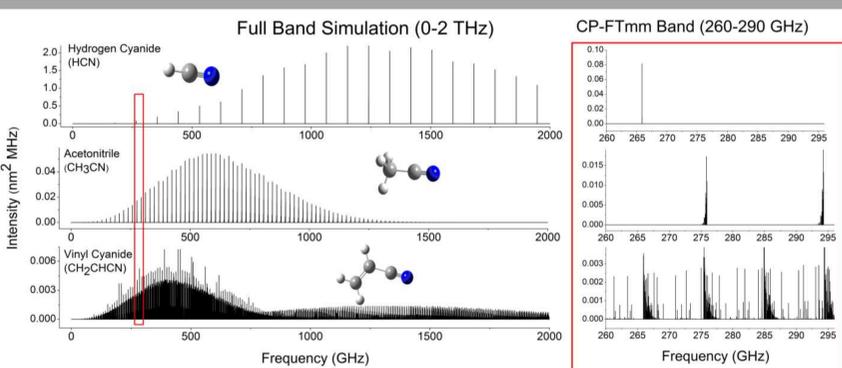


Schottky Diode Multiplier chains:

- Input frequency and bandwidth 2 – 4 GHz
- Output frequency and bandwidth 260 – 290 GHz
- 30mW power output sufficient for signal saturation.
- Frequency sweep keeps measurement below saturation limits (1000x sensitivity improvement over competing technology)¹



The AWG accomplishes the speed and phase reproducibility required for a chirped pulse measurement. In a segmented experiment, a two channel AWG generates a repeating excitation sweep (blue) and local oscillator continuous wave (red) that increase together in frequency with each segment. The intermediate frequency used for detection for each segment is from 720 – 1440 MHz.



A molecule's size and complexity affect the millimeter spectral density. CP-FTmm 260-290GHz offers sufficient bandwidth and sensitivity for the analysis of small volatile organic compounds (VOCs). The narrow line width (1.8 MHz) yields approximately 40,000 independent data channels.

Challenges

- 1) Broadband:** The need is for a practical, bench top spectrometer with broad chemical reach and detection accuracy. It will require > 10 GHz of spectral bandwidth.
- 2) Speed:** Coherent sub millimeter free induction decay lasts < 2µs requiring fast, phase reproducible excitation and measurement.
- 3) Low frequency digitization:** Real-time processing requires analogue to digital conversion below 2GHz, though the molecular emission is at 100s of GHz.

References and notes:

- 1) Steber A., Harris B., Neill J., Pate B., *J. Mol. Spec.*, 2012, **280**, 3
- 2) H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Muller, *J. Quant. Spectrosc. & Rad. Transfer*, 1998 **60**, 883
- 3) Toxicological Profile for Acrolein (CAS#: 107-02-8): Agency for Toxic Substances & Disease Registry
- 4) California proposition 65, Office of Environmental Health Hazard Assessment NSRL