Tokushima University

デュアルTHzコム分光法

徳島大学ポストLEDフォトニクス研究所（pLED）
安井 武史

分子研セミナー@2022/6/30

Tokushima University

Outline

1. Introduction
2. Dual THz comb spectroscopy (THz-DCS)
3. Gapless THz-DCS
4. Adaptive sampling THz-DCS using a single, free-running fiber laser
5. Summary

Tokushima University

Outline

1. **Introduction**
2. Dual THz comb spectroscopy (THz-DCS)
3. Gapless THz-DCS
4. Adaptive sampling THz-DCS using a single, free-running fiber laser
5. Summary

Sensing of gas mixed with aerosols

Enclosed space filled with smoke

Inflammable gas
Poisonous gas

Fire accident

Industry

Burning process

Combustion gas mixed with smoke and/or soot

Atmospheric analysis

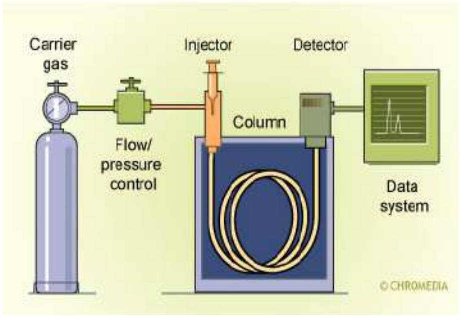
Exhaust gas, VOC
Mixed with SPM&PM

Gas analysis

- ✓ Multiples gasses
- ✓ Various aerosols
- ✓ Real time
- ✓ No sample preparation

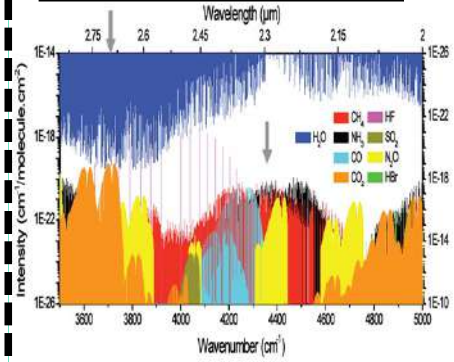
Conventional methods for gas analysis

Gas chromatography



High sensitivity, high resolution
Limited multiple analysis
Sample preparation
Long analysis time

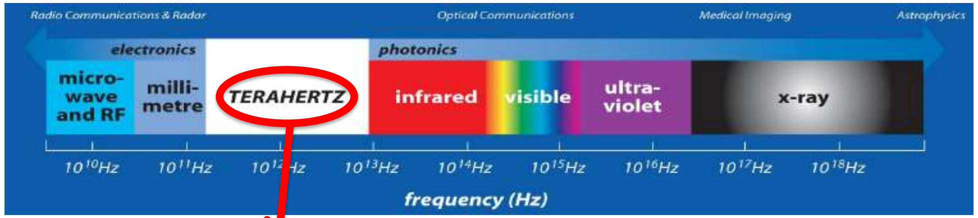
Infrared spectroscopy



Real time
Multiple gas analysis
No sample preparation
Sensitive to scattering

Tokushima University

Terahertz radiation



- both characteristics of optical and electric waves
- coherent beam
- low invasion
- less scattering
- good penetration
- THz spectral fingerprints

Tokushima University

THz spectroscopy of gases

(1) Rotational transitions of polar molecules

- ✓ Rich spectral fingerprints with high sensitivity
- ✓ High molecular selectivity based on rotational transition
- ✓ High molecular discrimination at low pressure due to narrow Doppler linewidth (~1MHz)

(2) Less scattering

- ✓ λ_{THz} >> particle diameter
- ✓ Possible to analyze gas molecules mixed with aerosols, fog, cloud, smoke, soot, etc

Tokushima University

THz spectroscopy of gases

(1) Rotational transitions of polar molecules

- ✓ Rich spectral fingerprints with high sensitivity
- ✓ High molecular selectivity based on rotational transition
- ✓ High molecular discrimination at low pressure due to narrow Doppler linewidth (~1MHz)

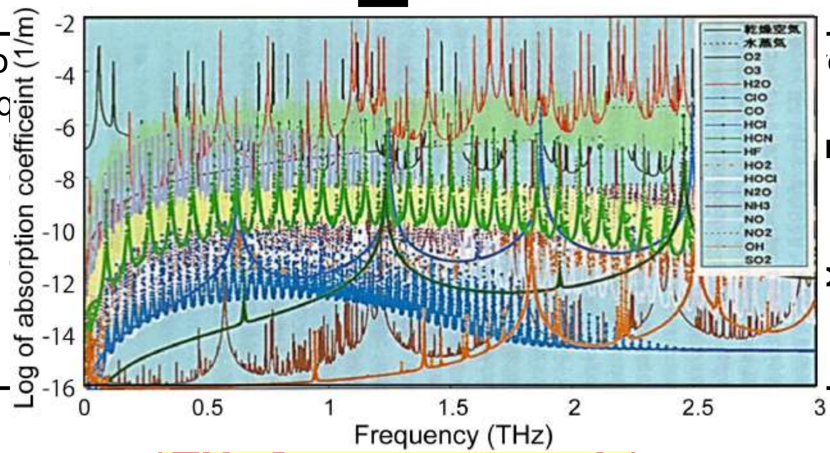
(2) Less scattering

- ✓ λ_{THz} >> particle diameter
- ✓ Possible to analyze gas molecules mixed with aerosols, fog, cloud, smoke, soot, etc

To discriminate the target gas correctly, high resolution, high accuracy, and broad spectrum are required simultaneously in THz region!

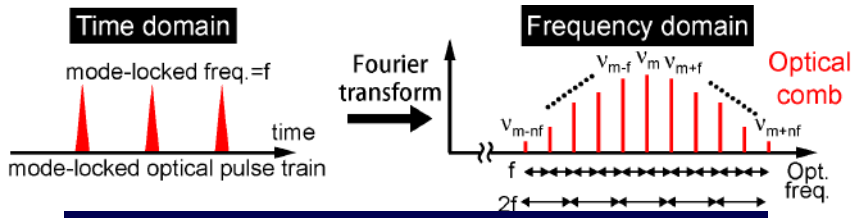
Co
req
➤
➤

ee
nd
ble

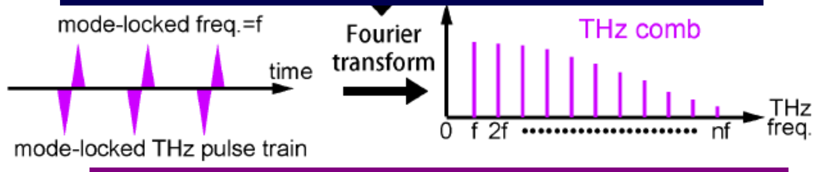


THz frequency comb

Optical comb and THz comb



Precise frequency marker for broadband THz spectrum



Simple, broadband selectivity, high spectral purity, and absolute frequency calibration

Tokushima University

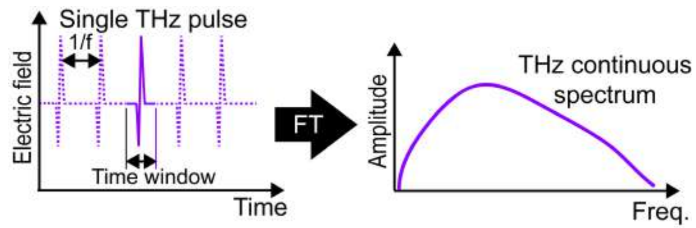
Outline

1. Introduction
2. **Dual THz comb spectroscopy (THz-DCS)**
3. Gapless THz-DCS
4. Adaptive sampling THz-DCS using a single, free-running fiber laser
5. Summary

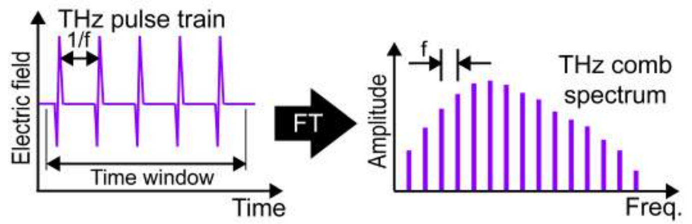
How measure mode-resolved THz comb spectrum?

Ref) IEEE Trans. THz Sci. Tech. ***3****, pp. 322-330 (2013).*

Traditional THz-TDS equipped with mechanical time-delay scanning

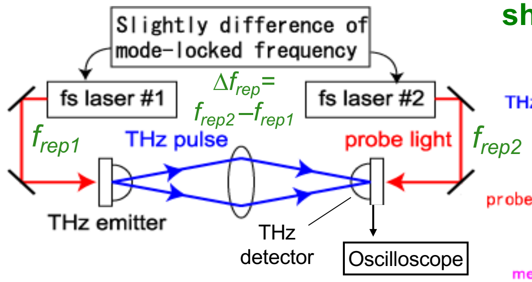


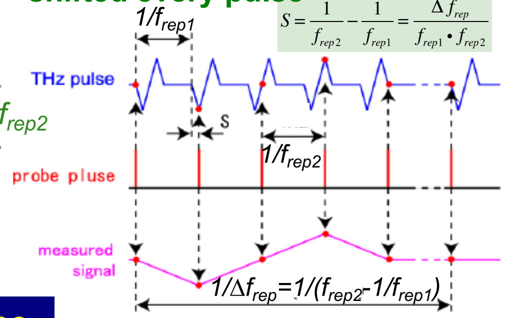
Time-window-extended THz-TDS



Asynchronous-optical-sampling THz-TDS (ASOPS-THz-TDS)

Overlap timing between THz and probe pulses is automatically shifted every pulse



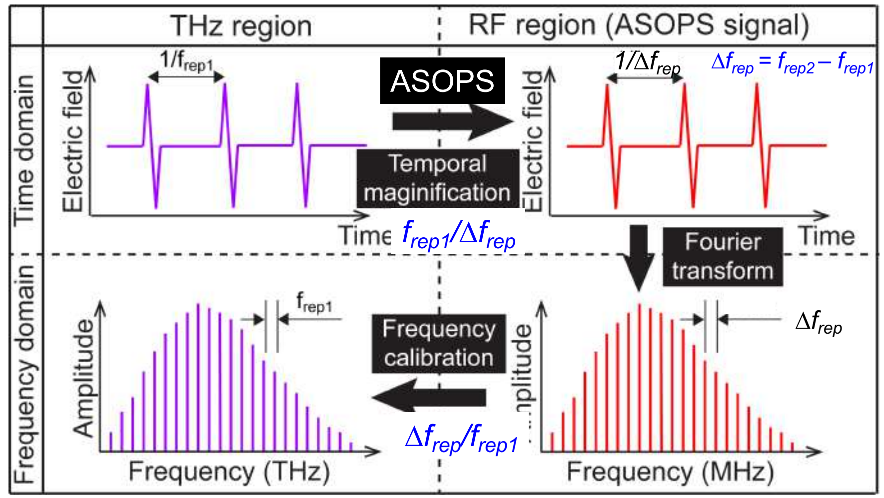


ref) T. Yasui, Appl. Phys. Lett. **87**, 061101 (2005).

- **No need for mechanical time-delay scanning**
- **No limitation for size of time window**

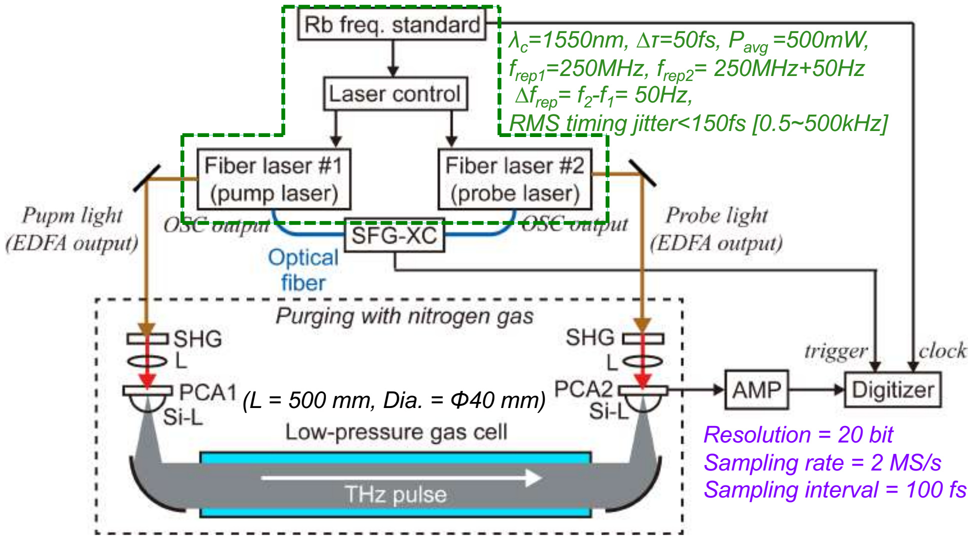
Time scale of ps THz pulse is linearly expanded to μs order

Signal flowchart in THz-DCS

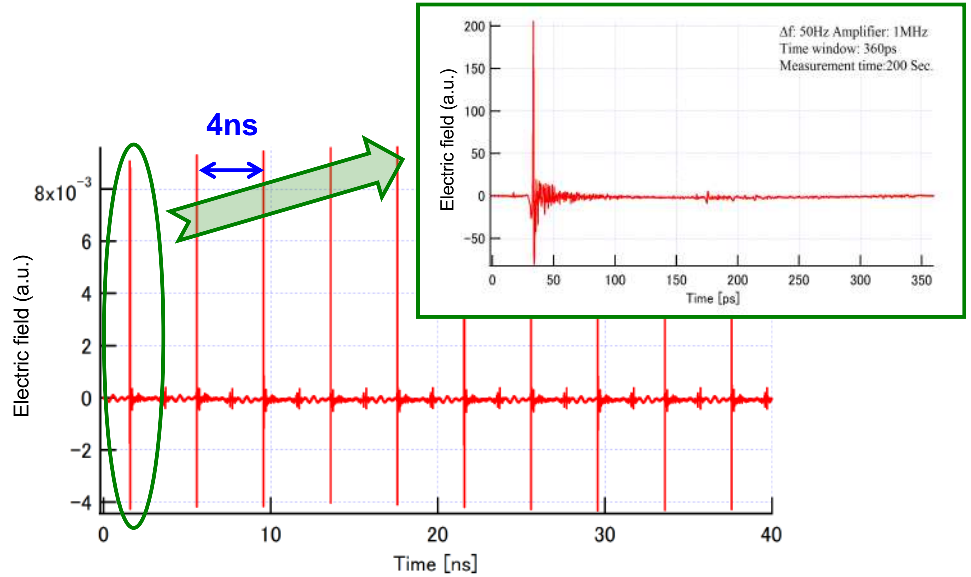


Experimental setup

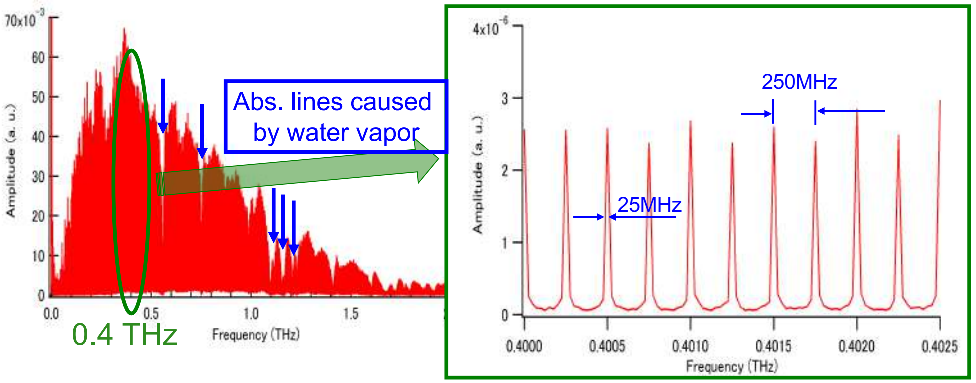
Ref) IEEE Trans. THz Sci. Tech. **3**, pp. 322-330 (2013).



Temporal waveform of 10 consecutive THz pulses



Mode-resolved THz comb spectrum

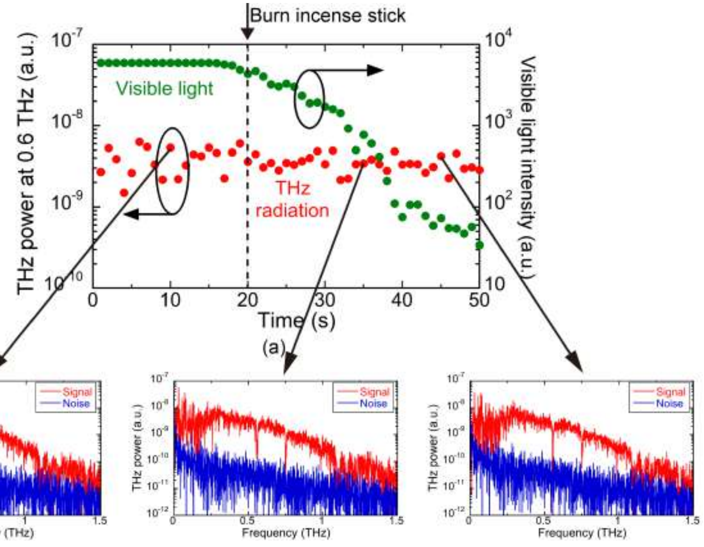


Frequency spacing = 250MHz = mode-locked frequency
Mode linewidth = 25 MHz = inverse of time window

Immunity to smoke scattering

Comparison of power between THz radiation and visible light

Pressure: atmospheric pressure
Gas cell: Φ50mm 200mm length



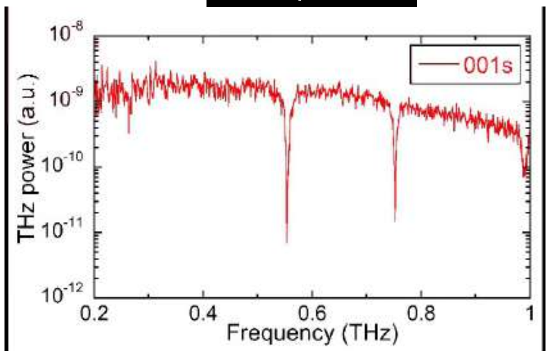
Dynamic THz spectroscopy

Measurement rate = 1 Hz

Experimental procedure

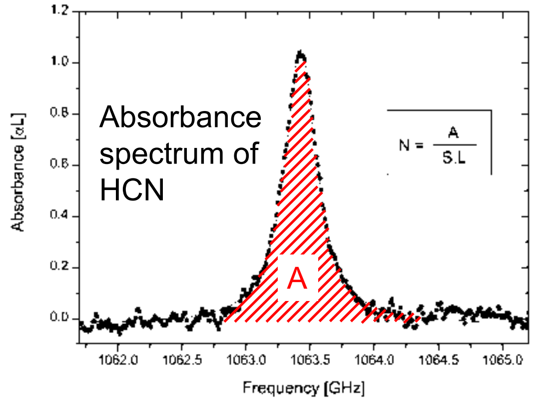
Pressure: atmospheric pressure
Gas cell: Φ50mm 200mm length
(1) Gas cell was filled with smoke.
(2) CH_3CN liquid droplet was put into the cell.
(3) CH_3CN liquid was evaporated.
(4) CH_3CN gas was diffused.

THz spectrum



Tokushima University
pLED 徳島大学ポストLEDフォトニクス研究所

Quantitative analysis of gas concentration



Fitting analysis considering all pressure-broadening absorption lines (> 400 lines)

Curve fitting with Lorentzian function

$$\alpha(\nu)L = \frac{A}{\pi}\left[\frac{\Delta\nu}{(\nu-\nu_0)^2+\Delta\nu^2}\right]$$

$$N = \frac{A}{SL}$$

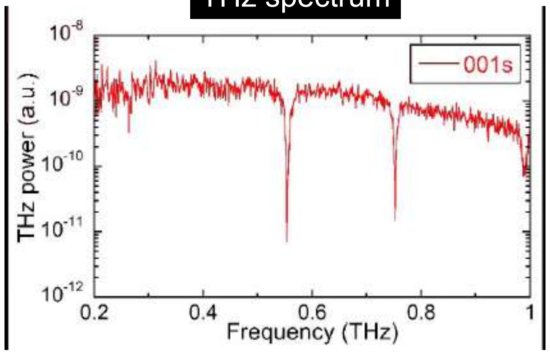
N: concentration (molecules/cm³)
A: line area
S: line intensity
L: interaction length

Ref) F. Hindle, C. R. Phys. **9**, 262–275 (2008).

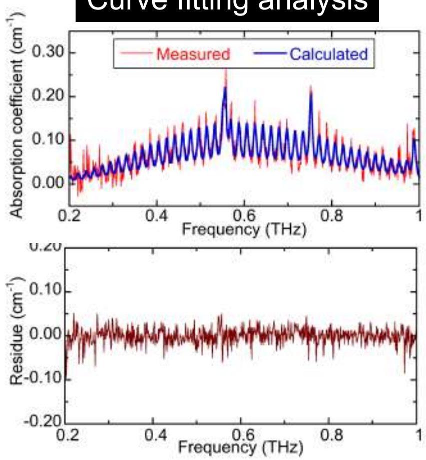
Dynamic THz spectroscopy

Measurement rate = 1 Hz

THz spectrum

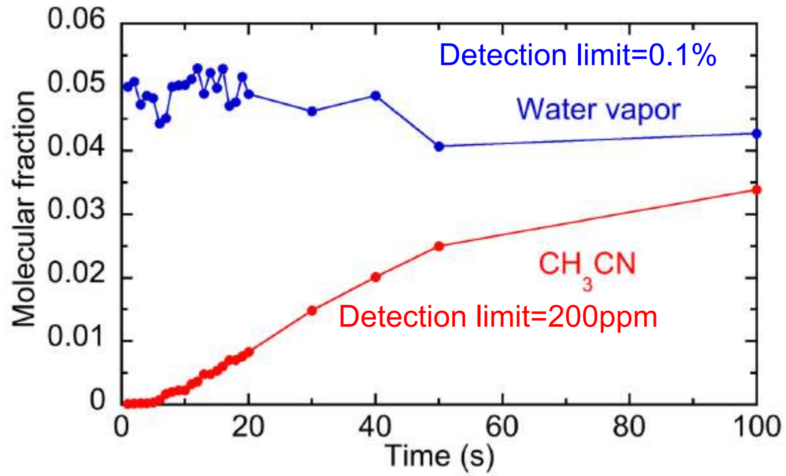


Curve fitting analysis



Fitting analysis of all absorption lines of CH_3CN and H_2O

Temporal change of gas concentration



Tokushima University

Detection limit of other gasses

(measurement rate = 1Hz)

Molecule	Number of absorption lines	Total integrated intensity (nm^2MHz)	Estimated detection limit
CH_3CN	900	7.5	200 ppm
CO	7	0.0082	18%
NO_2	3220	0.045	3%
HCN	9	7.9	200 ppm
HCl	2	0.10	1.5%
SO	135	2.4	600 ppm
SO_2	2397	2.0	700 ppm

Tokushima University

Outline

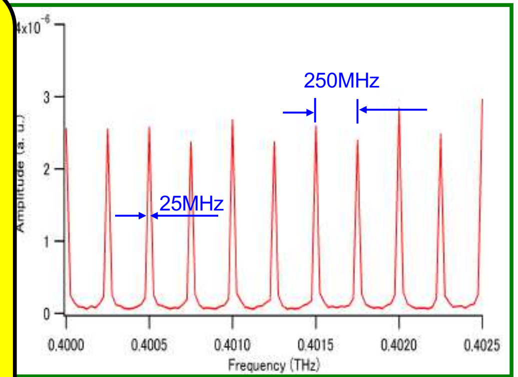
1. Introduction
2. Dual THz comb spectroscopy (THz-DCS)
3. **Gapless THz-DCS**
4. Adaptive sampling THz-DCS using a single, free-running fiber laser
5. Summary

Mode-resolved THz comb spectrum

Comb mode can be used as a frequency marker for broadband spectrum

Spectral sampling interval = frequency spacing

Mode linewidth << Frequency spacing



Hz = mode-locked frequency
Mode linewidth = 25 MHz = inverse of time window

Interleave additional frequency marks into frequency gap

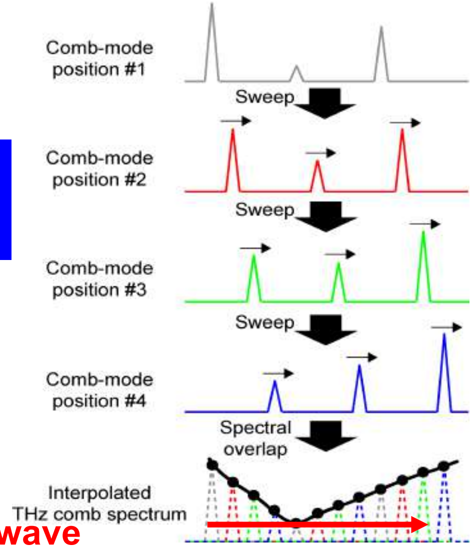
*Ref) Sci. Rep. **4**, 3816 (2014).*
*Optica **2**, 460-467 (2015).*

f_{rep1}, f_{rep2} : sweep
Δf_{rep} : constant

- Incremental sweeping at intervals of linewidth of comb mode
- Overlapping of all spectra

Gap between comb mode can be fully filled!

Equivalent to continuous sweeping of single CW-THz wave



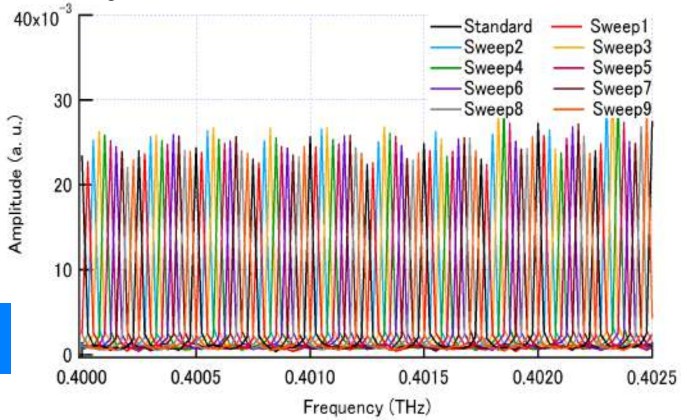
Sweep of THz comb mode by changing of ML frequency in dual fiber lasers

Before sweeping
f_{rep1}=250,000,049 Hz
f_{rep2}=250,000,099 Hz
Δf_{rep}=50Hz

f_{rep1} & f_{rep2} +15,625 Hz

Δf_{rep}: constant

Incremental sweeping is repeated 10-time

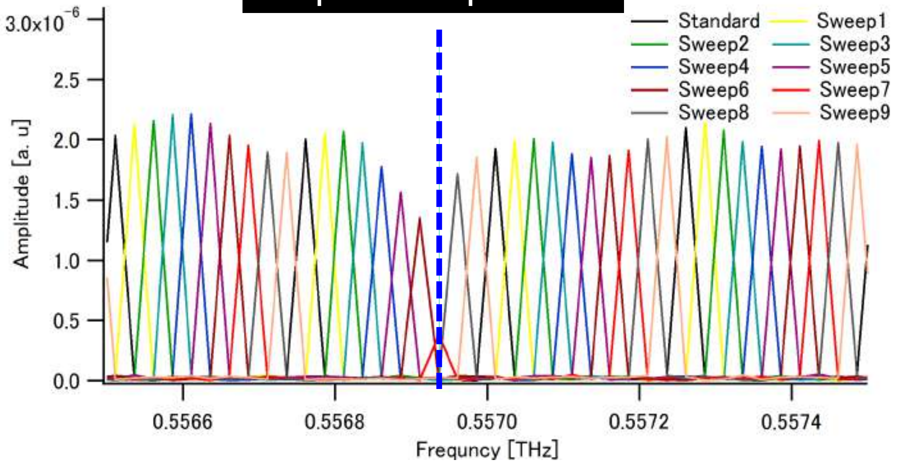


Frequency gaps between comb modes are fully filled!
Gap-less THz comb was achieved!

Spectroscopy of low-pressure water vapor

Rotational transition $1_{10} \leftarrow 1_{01}$: 0.5569360THz@NASA database
(Pressure broadening linewidth = 23 MHz @H_2O:10Pa&N_2:320Pa)

Amplitude spectrum



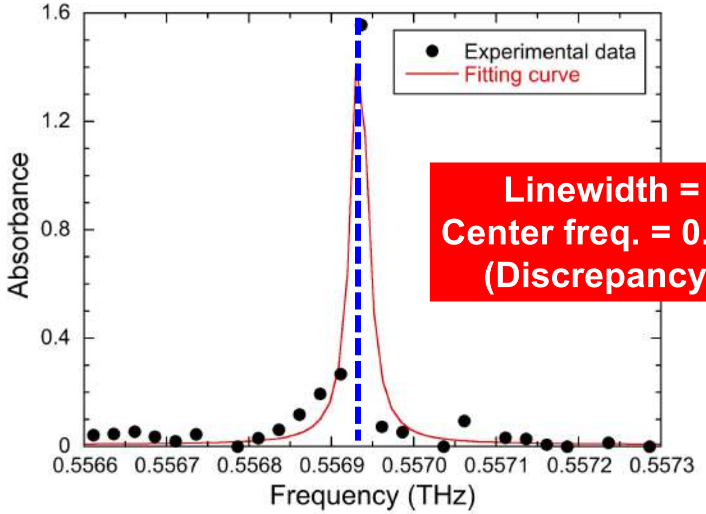
Tokushima University

pLED

Spectroscopy of low-pressure water vapor

Rotational transition $1_{10} \leftarrow 1_{01}$: 0.5569360THz@NASA database

(Pressure broadening linewidth = 23 MHz @H_2O:10Pa&N_2:320Pa)

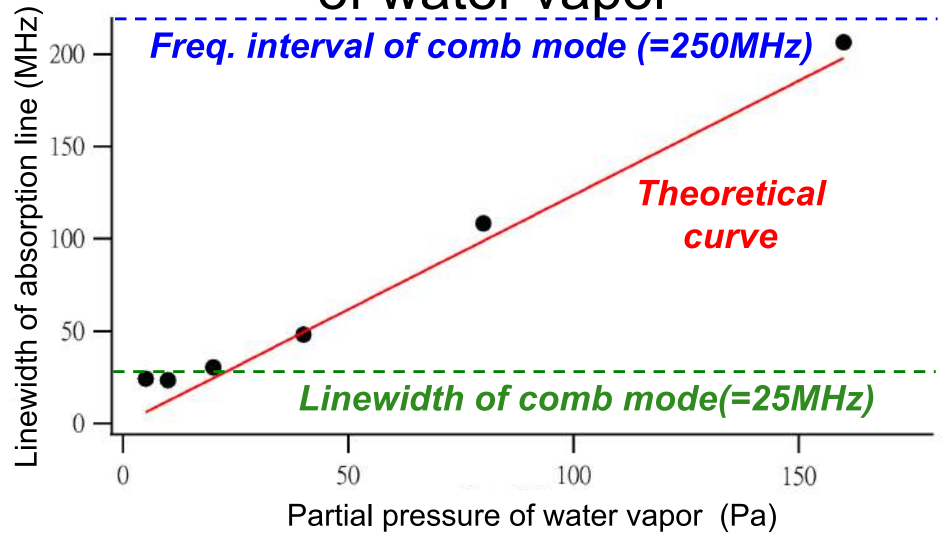


Linewidth = 24 MHz
Center freq. = 0.556930THz
(Discrepancy = 6MHz)

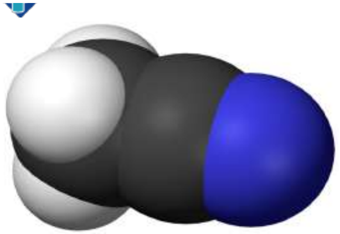
Tokushima University

pLED

Pressure broadening characteristic of water vapor

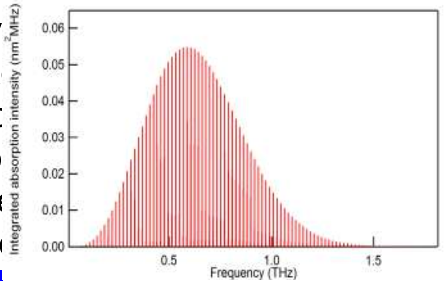


Sample : Acetonitrile (CH_3CN) gas



- ✓ Sy
- ✓ Int
- ✓ Inc
- ✓ Vo
- ✓ Bre
  es

s



Rotational transitions

$$\nu = 2B(J+1) - 2D_{JK}K^2(J+1)$$

B: rotational constant (= 9.194 GHz)
D_{JK}: centrifugal distortion constant (= 17.67 MHz)
J, K: rotational quantum numbers

Spectral signatures

1) A series of manifolds of rotational transitions regularly spaced by *2B*
2) Hyperfine structure of rotational transitions into each manifold determined by D_{JK}

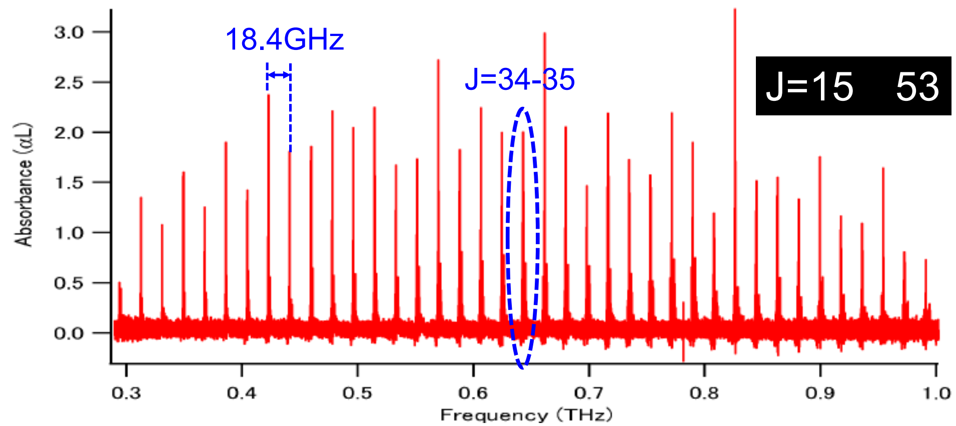
Tokushima University

pLED

Broadband spectroscopy of CH_3CN

Mode linewidth = sampling interval = 25 MHz

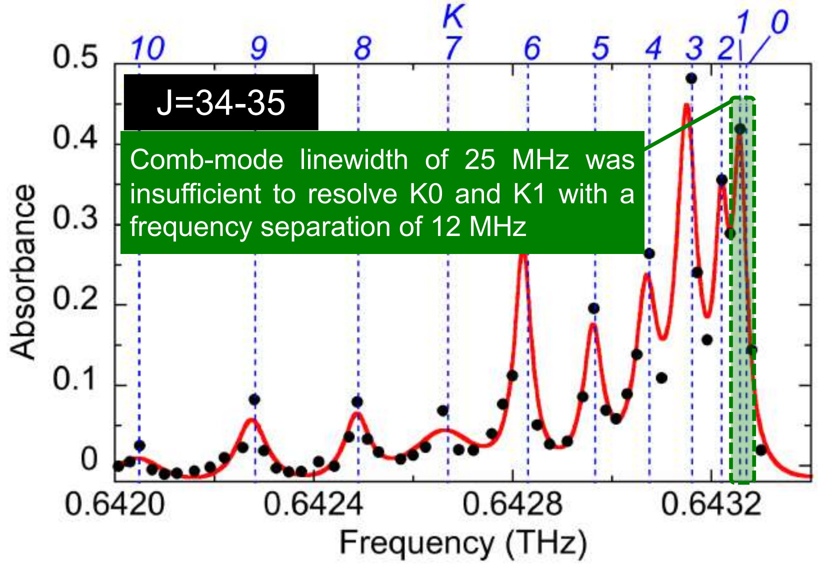
Gas pressure=40Pa



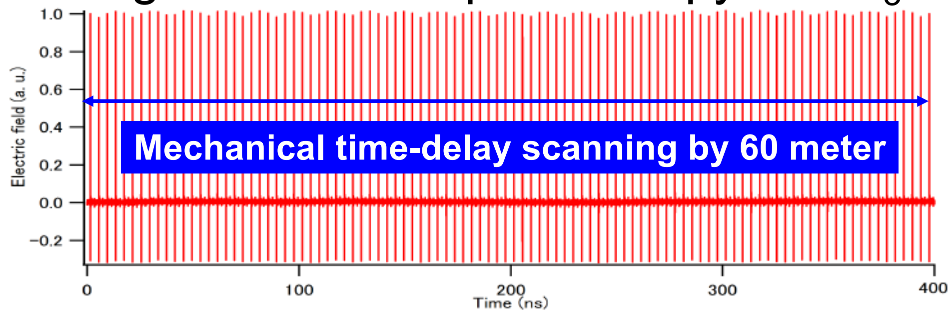
A series of rotational transition at interval of 2B (=18.4GHz)

High-resolution spectroscopy of CH_3CN

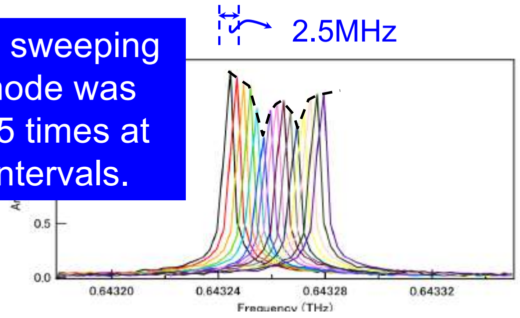
Mode linewidth = sampling interval = 25 MHz



Ultrahigh-resolution spectroscopy of CH_3CN

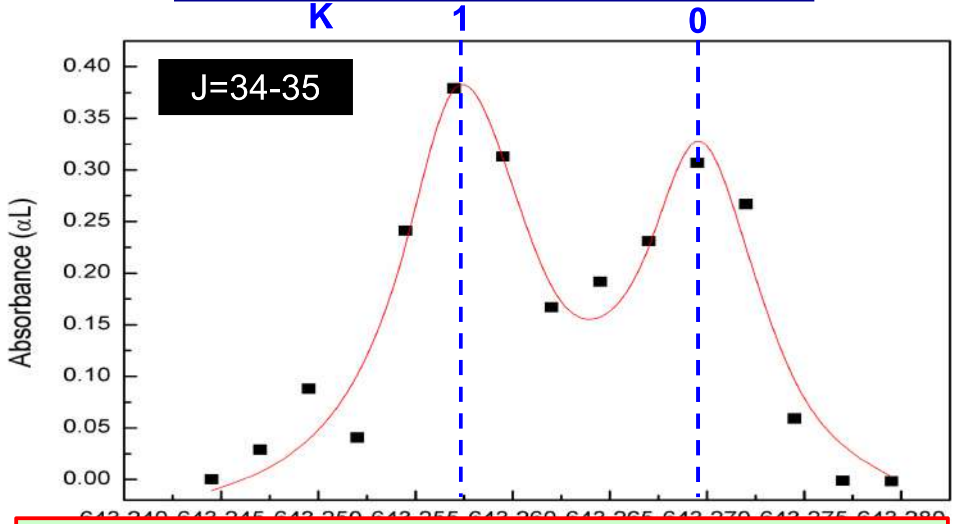


Incremental sweeping of comb mode was repeated 15 times at 2.5 MHz intervals.



Ultrahigh-resolution spectroscopy of CH_3CN

Mode linewidth = sampling interval = 2.5 MHz



Splitting due to centrifugal distortion characterized by D_{JK}

Tokushima University

Comparison of absorbance peak positions with NASA database in CH_3CN

Line number (K)	NASA database (THz)	Experimental value (THz)	Discrepancy (MHz)
10	0.642049	0.642046	3
9	0.642280	0.642276	4
8	0.642487	0.642488	1
7	0.642670	0.642664	6
6	0.642829	0.642821	8
5	0.642963	0.642961	2
4	0.643074	0.643068	6
3	0.643159	0.643150	9
2	0.643220	0.643216	4
1	0.643257	0.643257	0.62
0	0.643269	0.643269	0.26

Comb mode linewidth = sampling interval = 25MHz (K = 10–2)

Comb mode linewidth =sampling interval = 2.5MHz (K = 1–0)

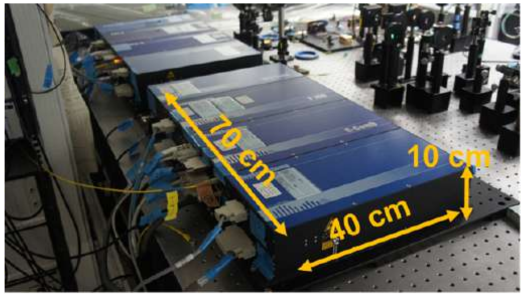
Corresponding to spectral accuracy of 10^{-7}

Outline

1. Introduction
2. Dual THz comb spectroscopy (THz-DCS)
3. Gapless THz-DCS
4. **Adaptive sampling THz-DCS using a single, free-running fiber laser**
5. Summary

Limiting factors for practical application

Dual stabilized fiber lasers



Laser stabilization system

(1)Use of dual fs lasers
➡ Single fs laser
(2)Precise stabilization of Δf_{rep}
➡ Free-running fs laser

How **dual** pulse lights with different f_{rep} can be generated by a **single** fs laser?

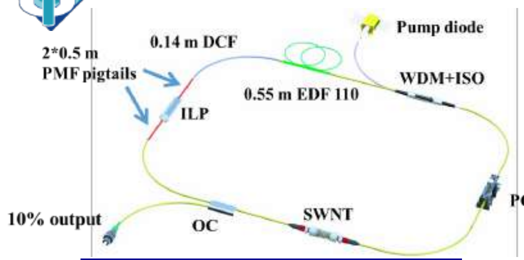
ANSWER

Dual-wavelength mode-locked Er-doped fiber laser

- ✓ Simultaneous and independent mode-locking of two different-wavelength lights in the same cavity
- ✓ Material dispersion in a fiber cavity makes f_{rep} a slightly different between two wavelength lights
- ✓ Share of the same cavity fluctuates f_{rep1} and f_{rep2} in the common-mode manner, leading to the stable Δf_{rep}

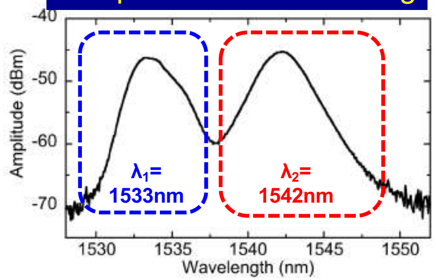
*Ref) Hu, CLEO-PR2015, 26A3_7; Sci. Rep. **7**, 42082 (2017)*

Dual-λ mode-locked Er-fiber laser



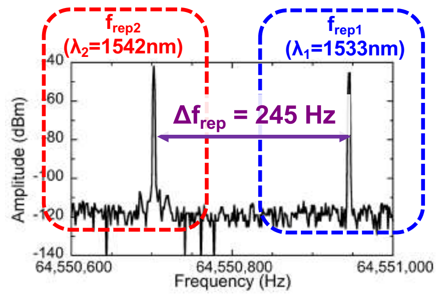
- ➢ Mode-locking by SWNT
- ➢ Dual-λ ML oscillation by Lyot filter and gain modulation

Independent mode-locking



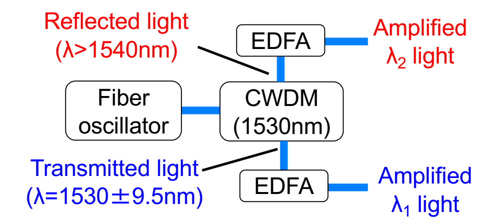
Optical spectrum

Slightly detuned f_{rep1} and f_{rep2}

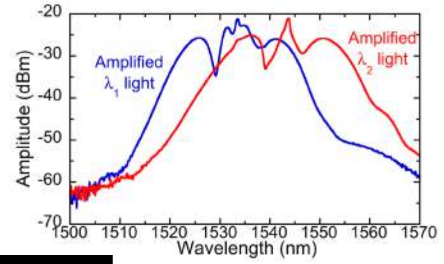


RF spectrum

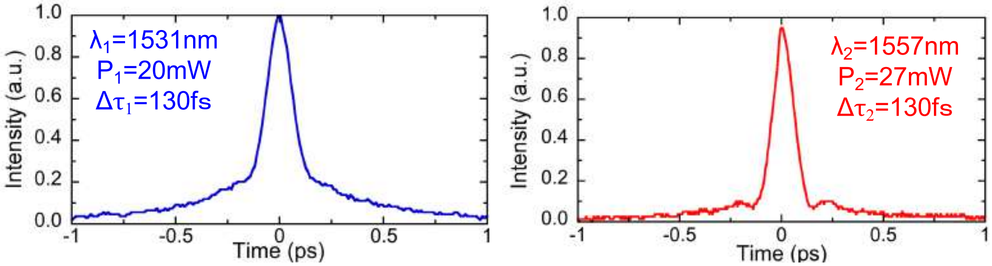
Separated and amplified dual-λ light



Optical spectrum

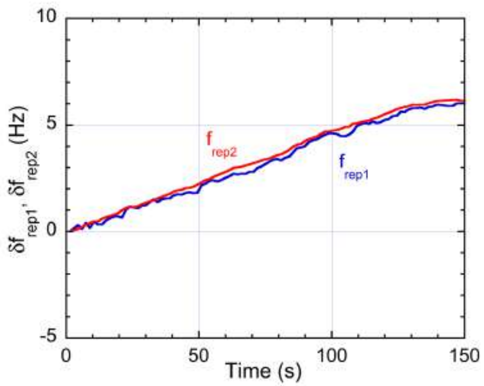


Autocorrelation trace

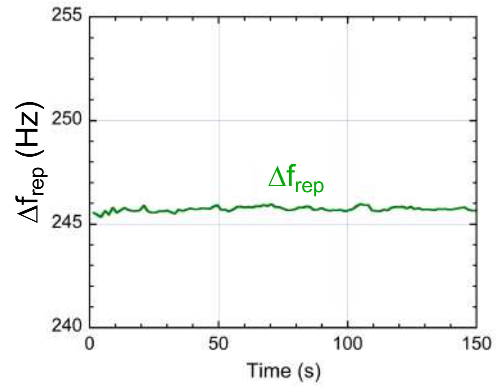


Characteristics of f_{rep1}, f_{rep2}, Δf_{rep}

Temporal change of f_{rep1} and f_{rep2}



Temporal change of Δf_{rep}



Stable Δf_{rep} without the need for active stabilization

Precisely stabilized, dual fs lasers have been used in previous researches of THz-DCS

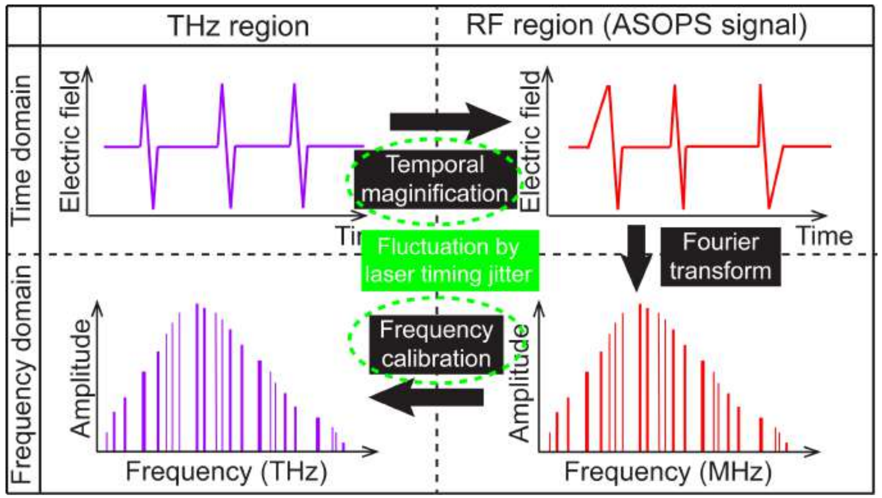
↓

Use of **free-running,** dual-λ mode-locked Er-fiber laser expands application fields of THz-DCS

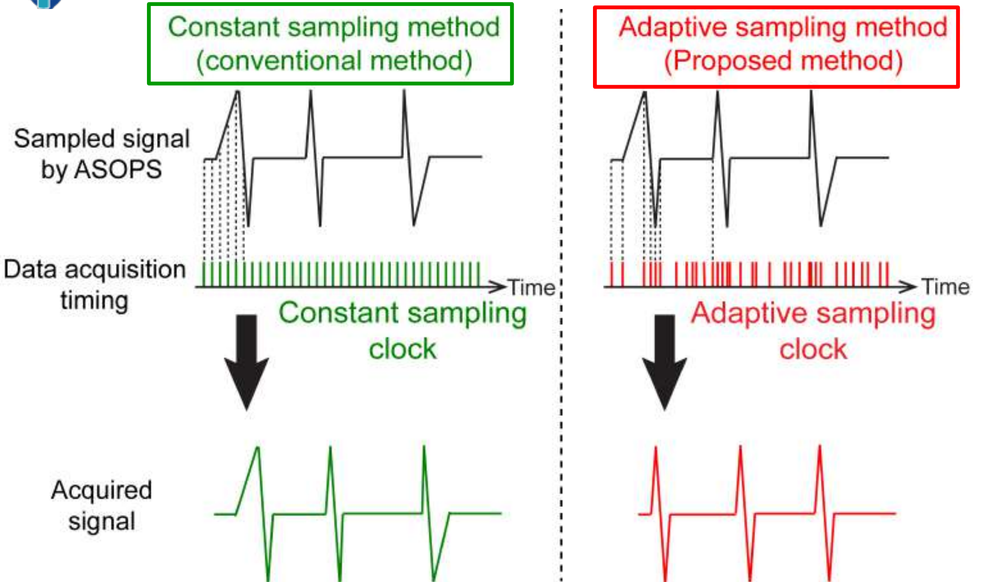
↓

However, influence of timing jitter between free-running dual lasers has to be considered!

Influence of timing jitter in THz-DCS



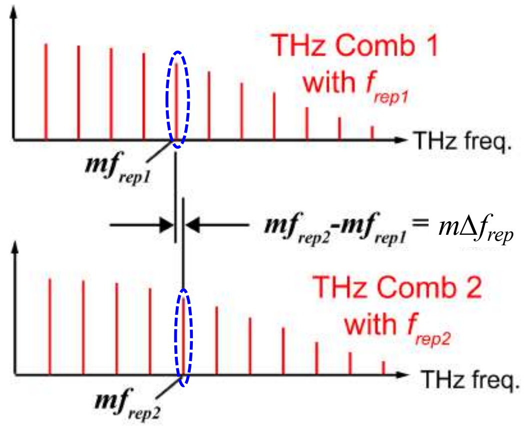
Adaptive sampling method



Ref) Ideguchi, Opt. Lett. ***37****, 4847 (2012); Ideguchi, Nat. Comm.* ***5****, 3375 (2014).*

Adaptive sampling clock for f_{rep}

Beat signal between dual THz combs, which is a harmonic component of Δf_{rep} (= $m\Delta f_{rep}$= mf_{rep2}-mf_{rep1}) !!



Comb mode is too dense and too weak!

↓

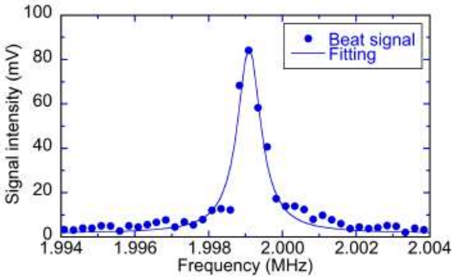
Difficult to extract a single mode from THz comb directly!

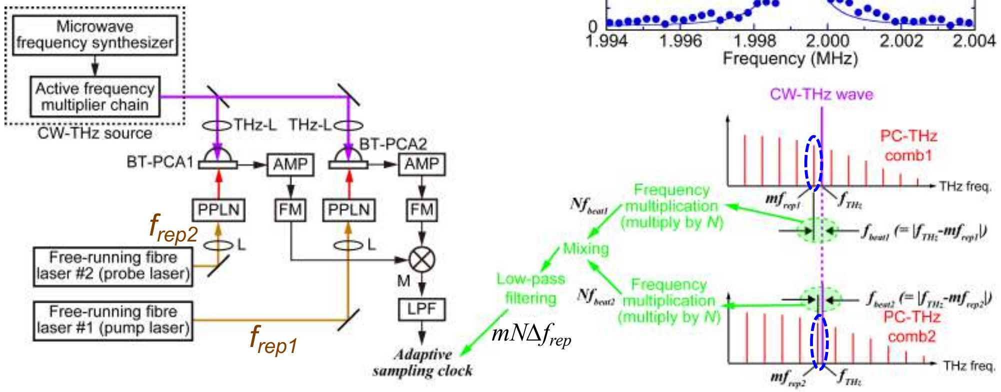
↓

Photoconductive mixing between CW-THz radiation and PC-THz comb

Ref) Yasui, Sci. Rep. ***5****, 10786 (2015).*

Adaptive sampling clock generator based on dual photoconductive mixing

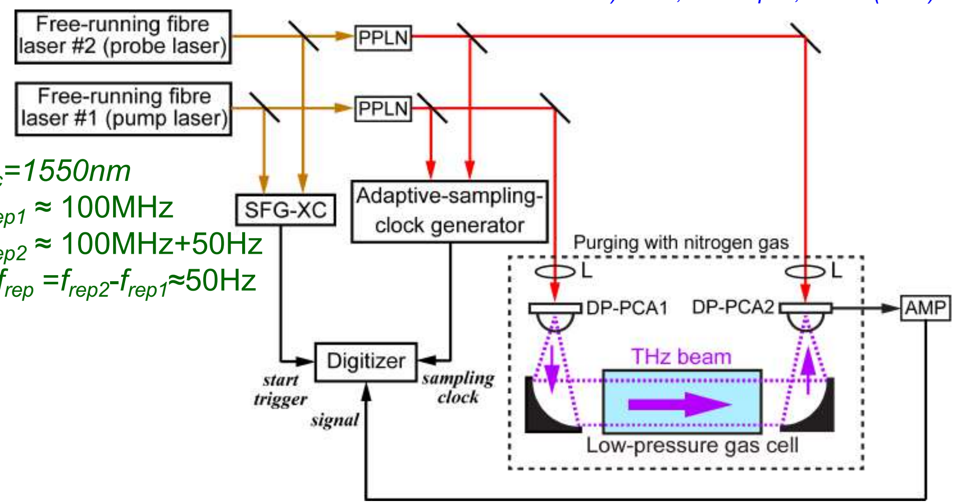




Ref) Yasui, Sci. Rep. ***5****, 10786 (2015).*

Experimental setup for THz-DCS

Ref) Yasui, Sci. Rep. ***5****, 10786 (2015).*



λ_c=1550nm
f_{rep1} ≈ 100MHz
f_{rep2} ≈ 100MHz+50Hz
Δf_{rep} =f_{rep2}-f_{rep1}≈50Hz

Integrated temporal waveform of THz pulse

(time window = 100 ns, sampling interval = 100 fs, integration number =10,000)

Ref) Yasui, Sci. Rep. ***5****, 10786 (2015).*

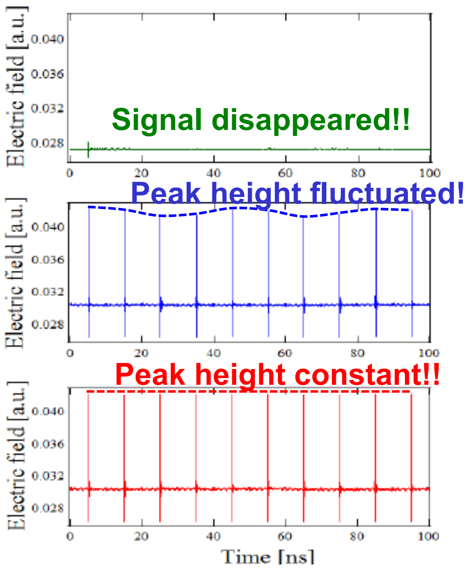
Constant sampling with free-running lasers

Constant sampling with stabilized lasers

RMS timing jitter (0.1 Hz-500 kHz) < 150 fs

Freq. ref.: Rb atomic clock (stability 10^{-11})

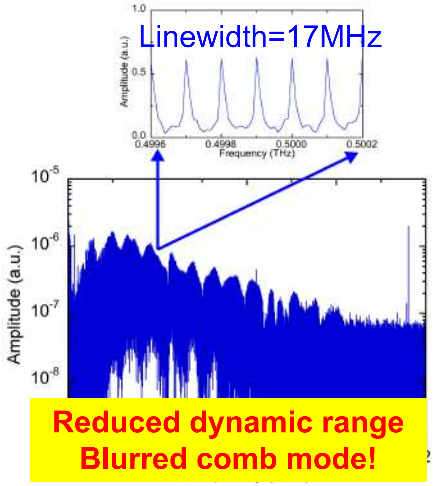
Adaptive sampling with free-running lasers

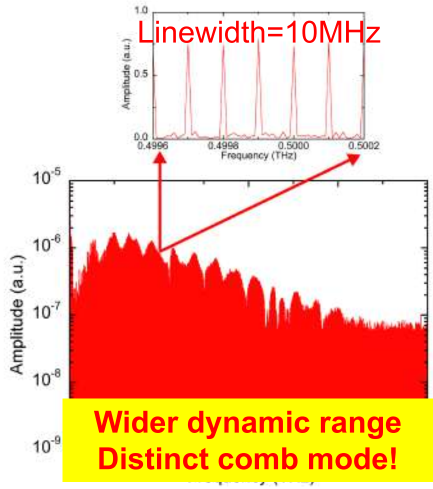


Mode-resolved THz comb spectrum

Constant sampling with stabilized lasers

Adaptive sampling with free-running lasers

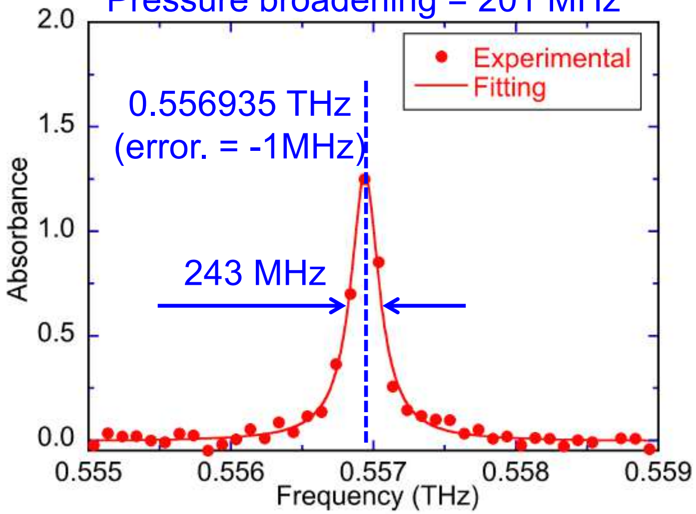




Low-pressure water vapor (145Pa)

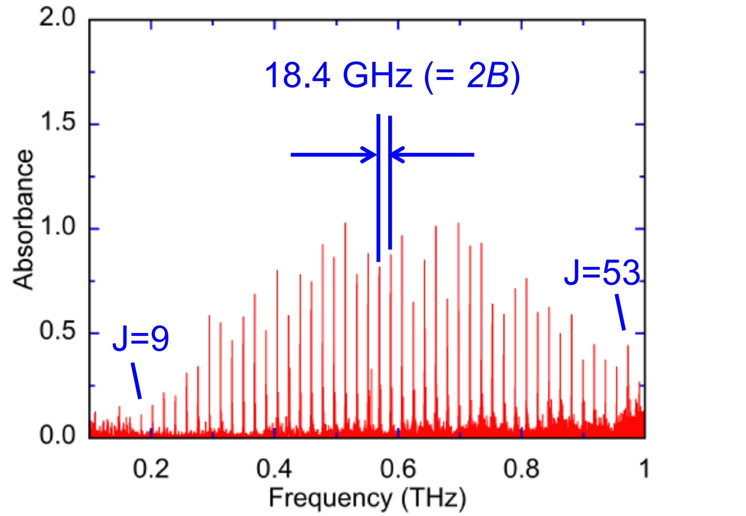
Asymmetric top molecule, $1_{10} \leftarrow 1_{01}$ @ 0.5569365 THz,

Pressure broadening = 201 MHz

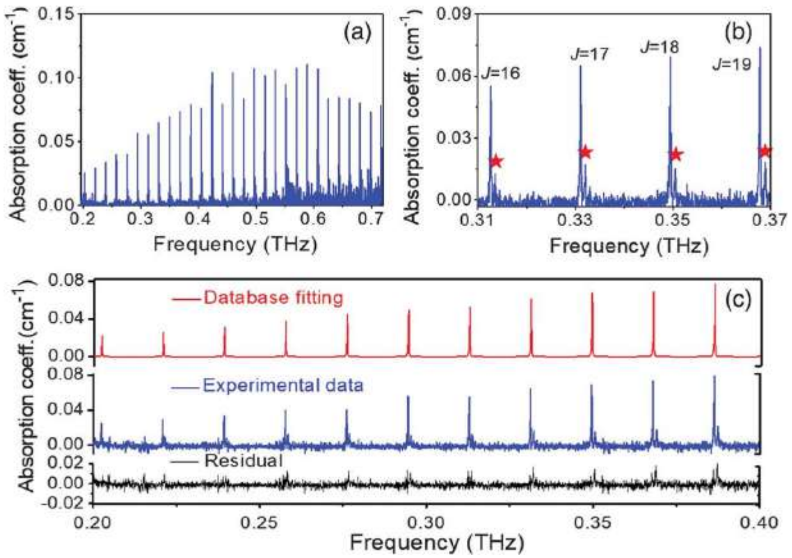


Acetonitrile gas at low pressure(1kPa)

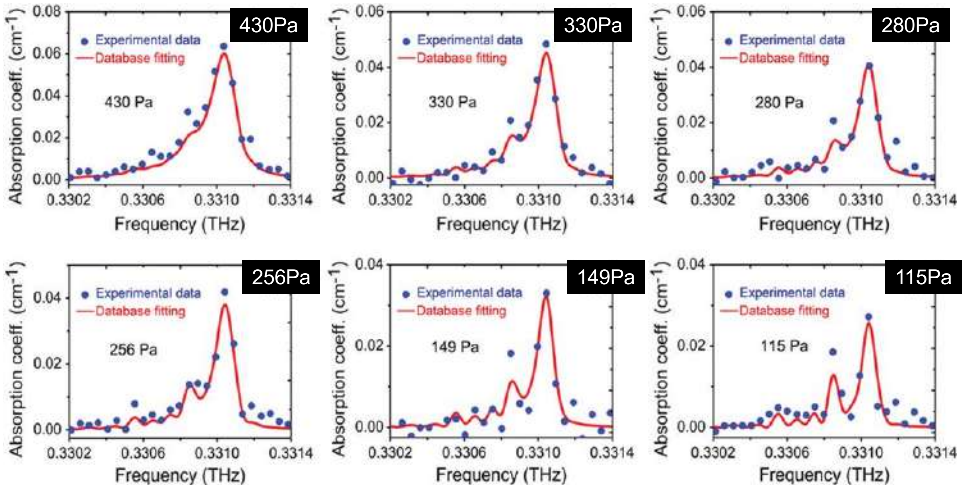
Symmetric molecule, rotational constant B = 9.2 GHz



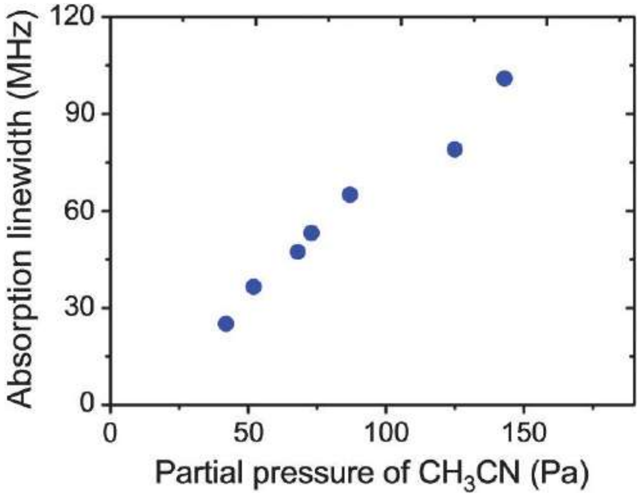
Comb-mode-resolved THz spectroscopy of a mixture gas sample of CH_3CN and air with a total pressure of 360 Pa



Mode-resolved absorption characterization of CH_3CN around 0.331 THz



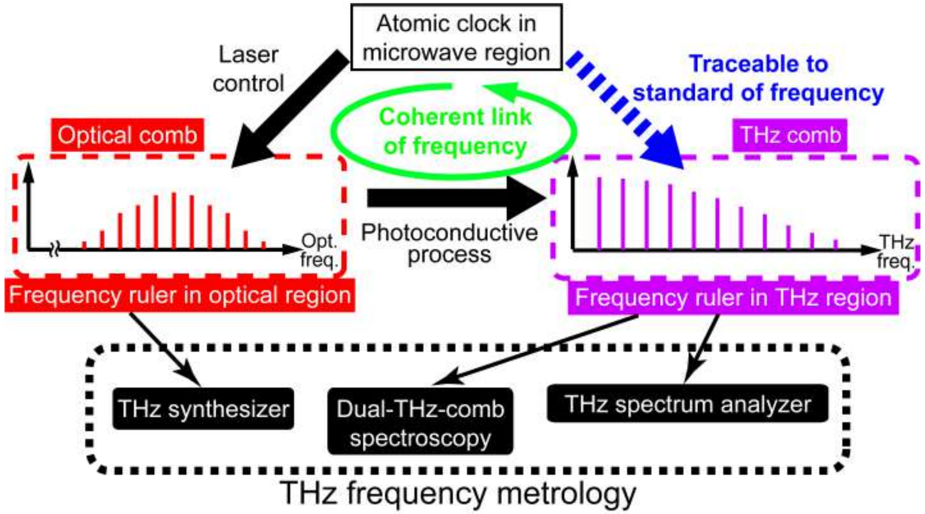
Pressure broadening characteristic of CH_3CN/air gas



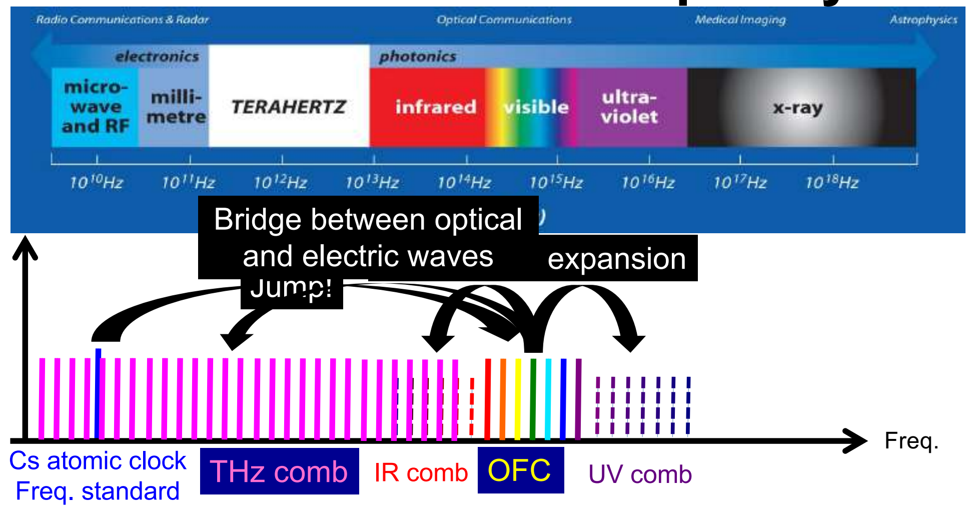
Outline

1. Introduction
2. Dual THz comb spectroscopy (THz-DCS)
3. Gapless THz-DCS
4. Adaptive sampling THz-DCS using a single, free-running fiber laser
5. **Summary**

THz frequency metrology based on frequency comb



Coherent link of frequency



It is possible to discuss frequencies with "same accuracy" beyond the boundaries of each electromagnetic region!