CLEO2014: STh1N.2

Spectrally Interleaved, Comb-Mode-Resolved, Dual-Terahertz-Comb Spectroscopy

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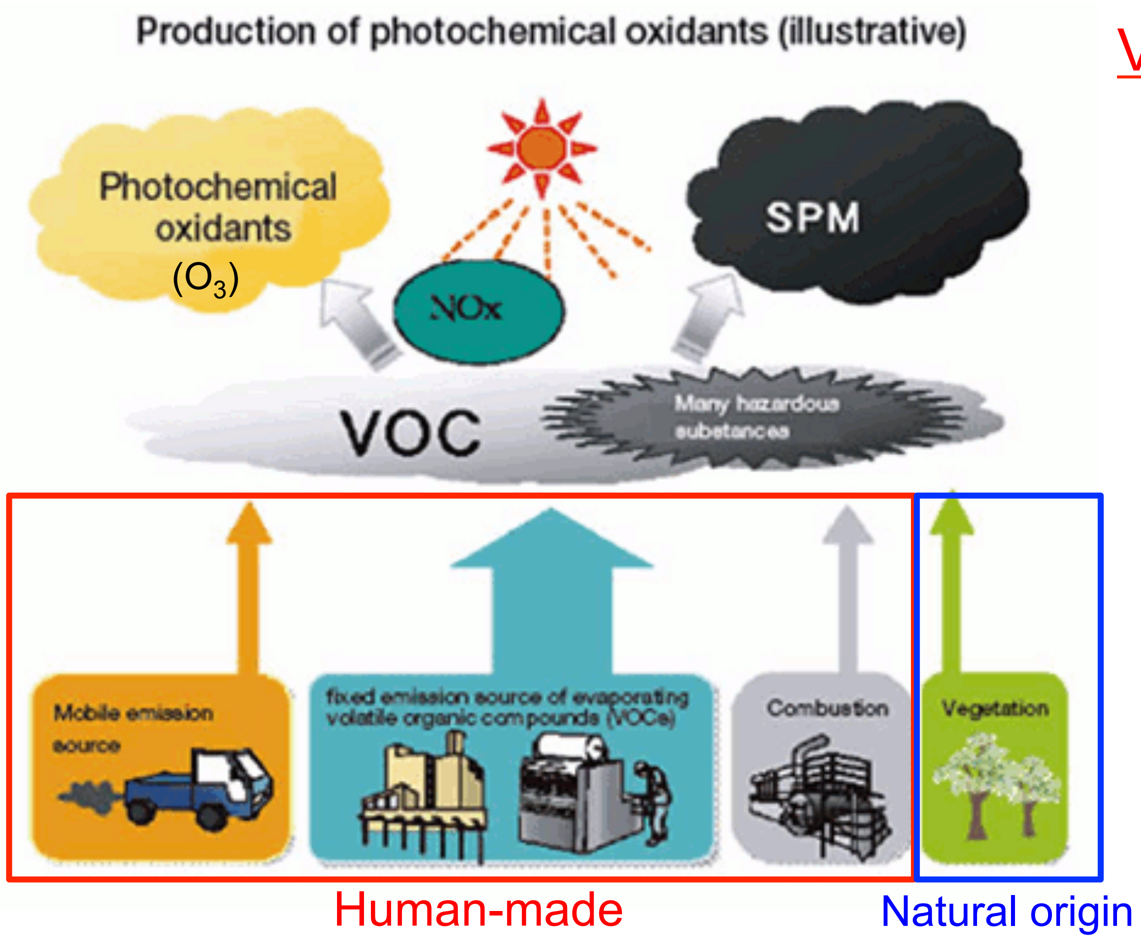
Air pollution by VOCs



From: Environment of Tokyo

Volatile organic compounds (VOCs)

VOC is the general term of organic compounds that become gaseous in the atmosphere

Photochemical reaction

Primary air pollutants

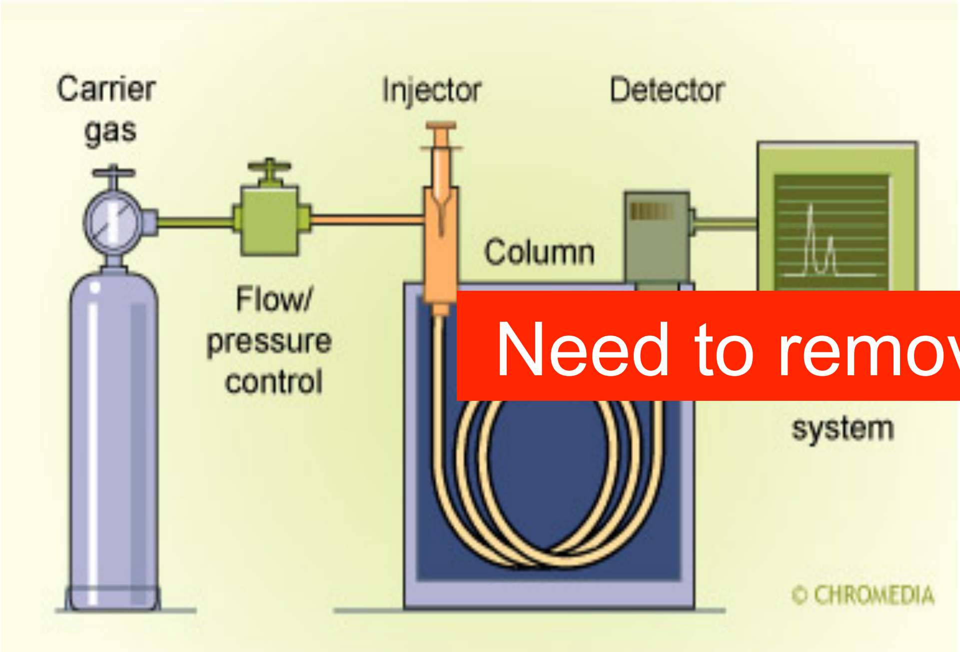
- Ozone (O_3)
- Small particulate matter (SPM)

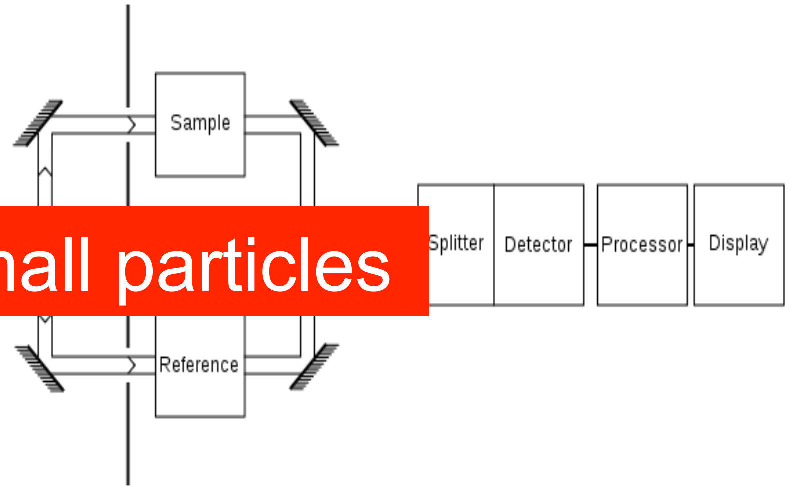
The instrumental analysis of VOC gases is important to pollution control !!

Conventional techniques

Gas chromatography

Infrared spectroscopy





Need to remove small particles

Form: http://www.chromedia.org/

Advantages: Excellent resolution, Sensitivity

Disadvantages: Need skilled instrumental analyst, Long measurement time

From: en.wikipedia.org

Advantages: High speed, Broadband spectrum

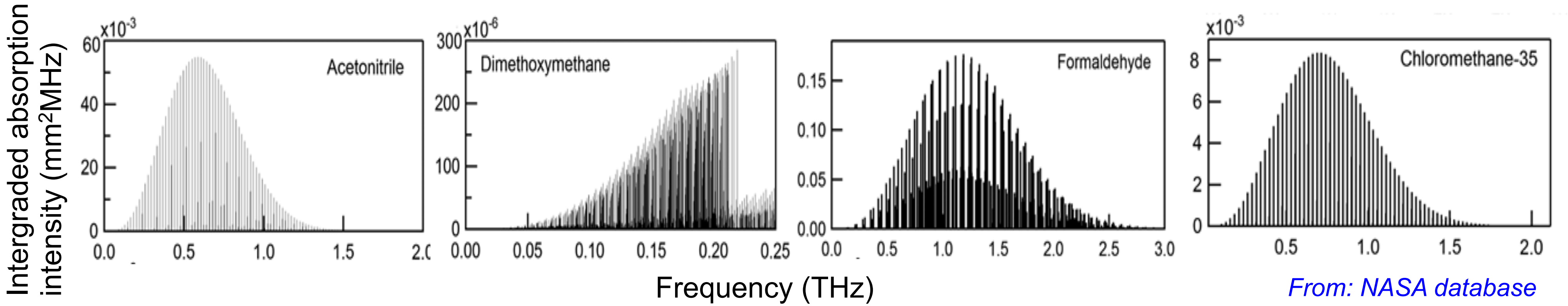
Disadvantages: Scattering by aerosol, Low sensitivity

With conventional techniques, it was difficult to analyze VOC gases directly without preparing samples in advance

THz gas spectroscopy

(1) Rotational transition of polar molecules

Rich spectral fingerprints, high discrimination, high sensitivity



From: NASA database

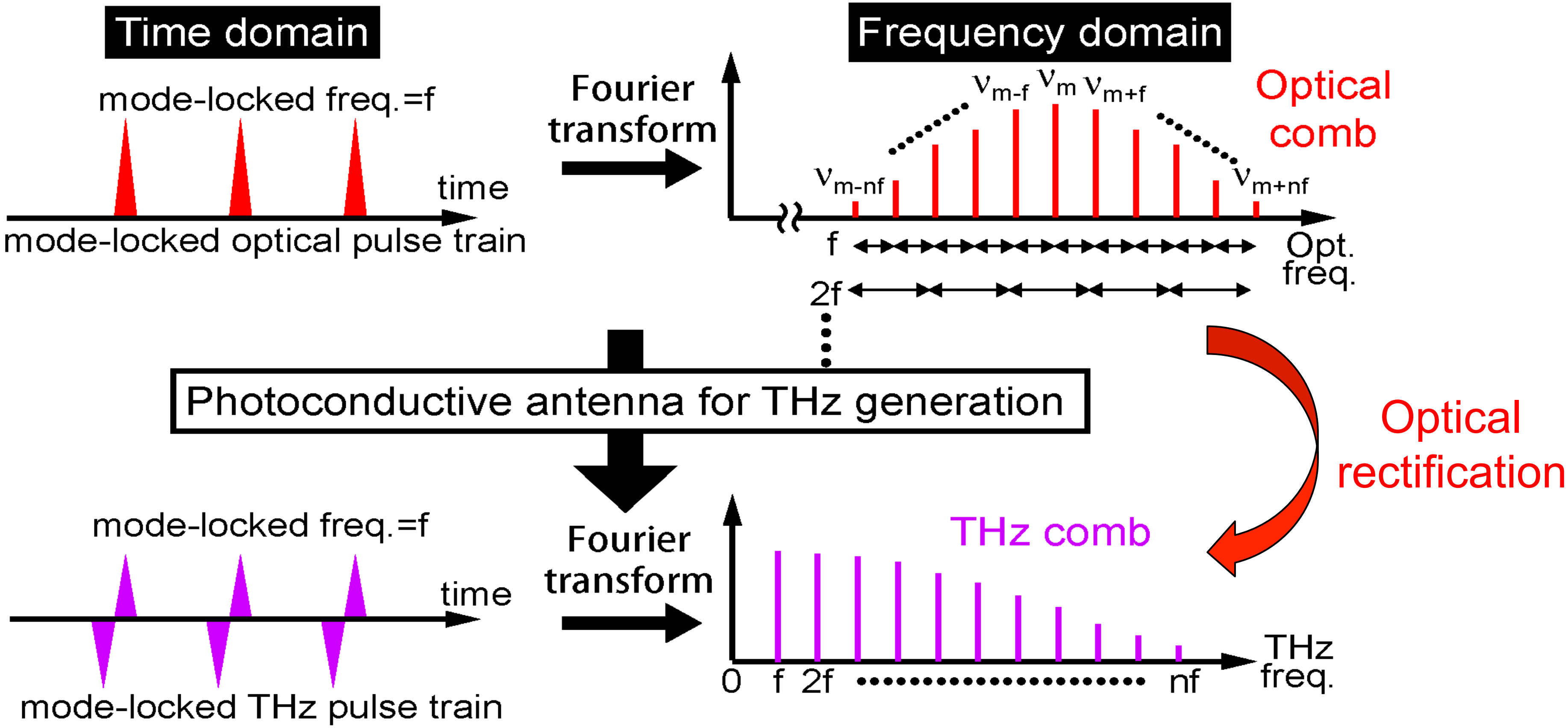
THz spectral fingerprints of VOC gases

(2) Reduced scattering in small particles

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

THz spectroscopy has high potential for analysis of VOC gas. However, **high accuracy**, **high resolution**, and **broadband spectrum** are required for correct discrimination!!

Optical comb & THz comb



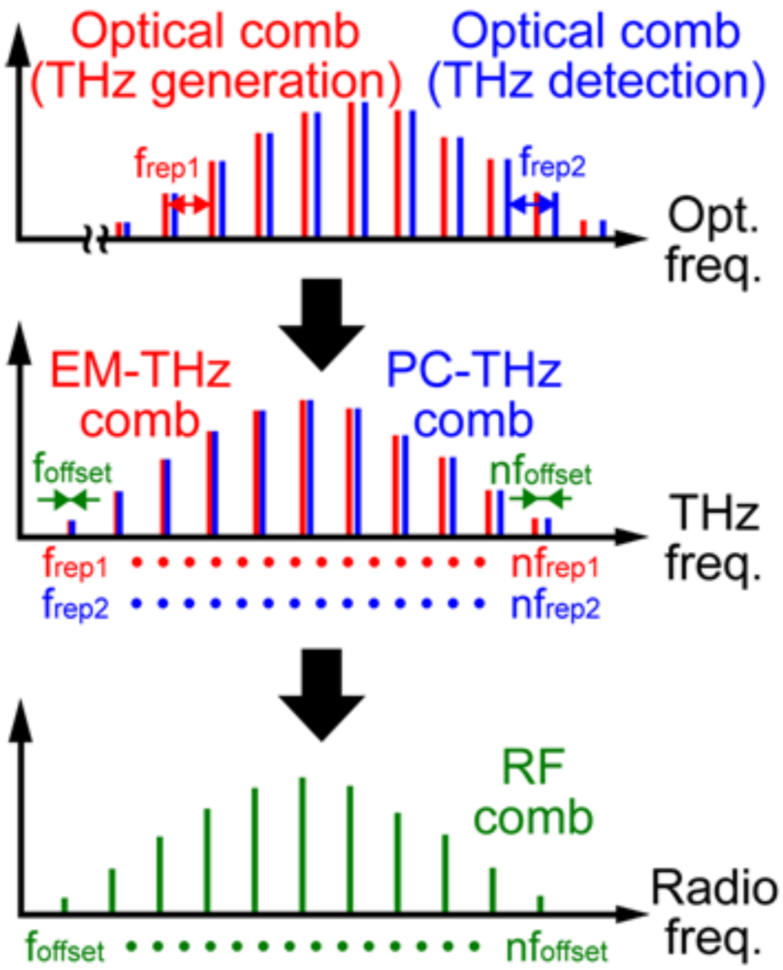
Precise frequency ruler in THz region!

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

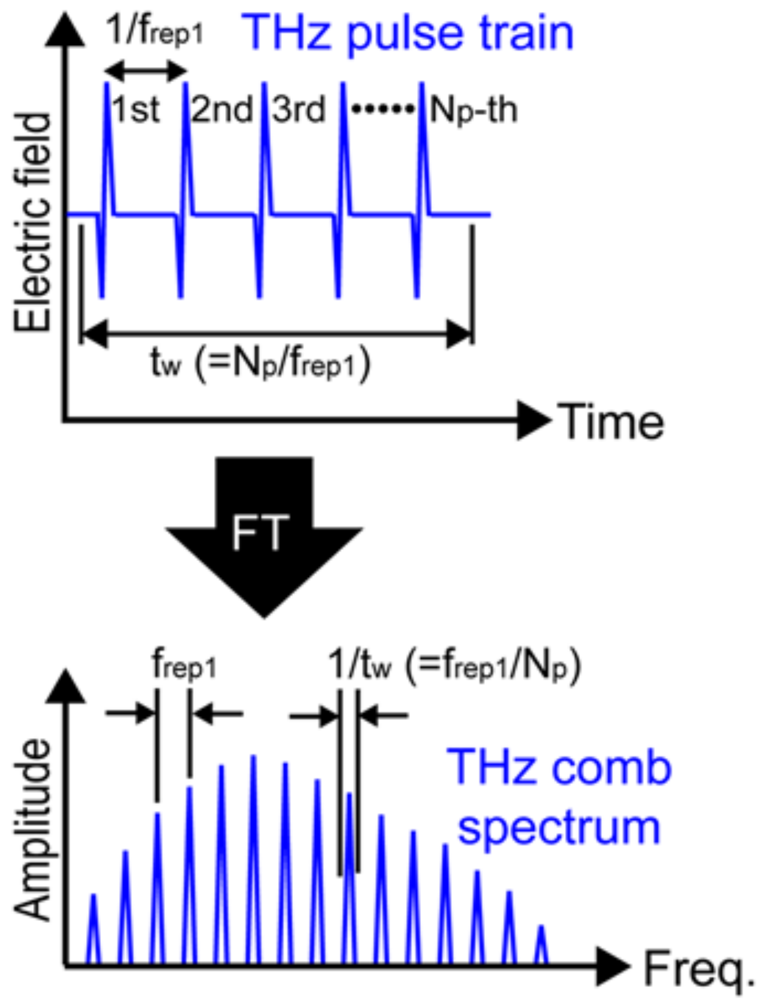
*Ref) T. Yasui, et al, IEEE J. Quantum. Electron., **17**, 191 (2011).*

Dual THz comb spectroscopy

Frequency domain



Time domain

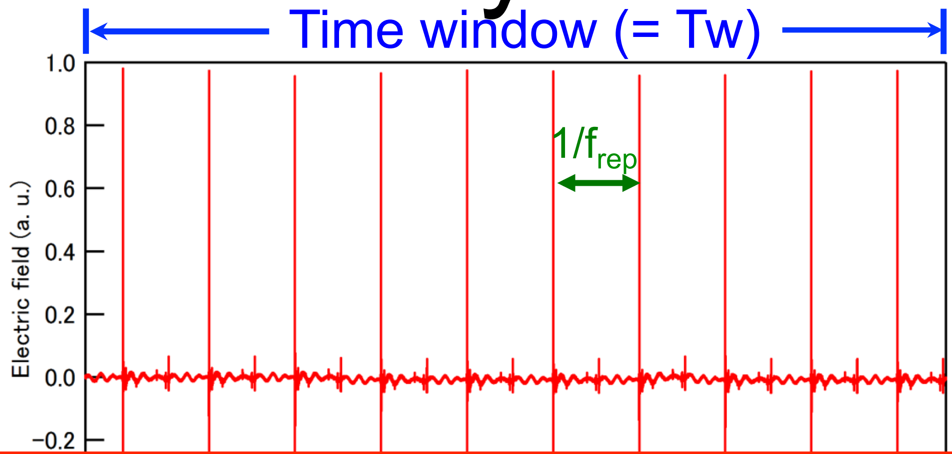


*Ref) T. Yasui, et al, Appl. Phys. Lett., **88**, 241104 (2006).*

Ref) Y. -D. Hsieh, et al, Sci. Rep., 4, 3816 (2014)

Previous study

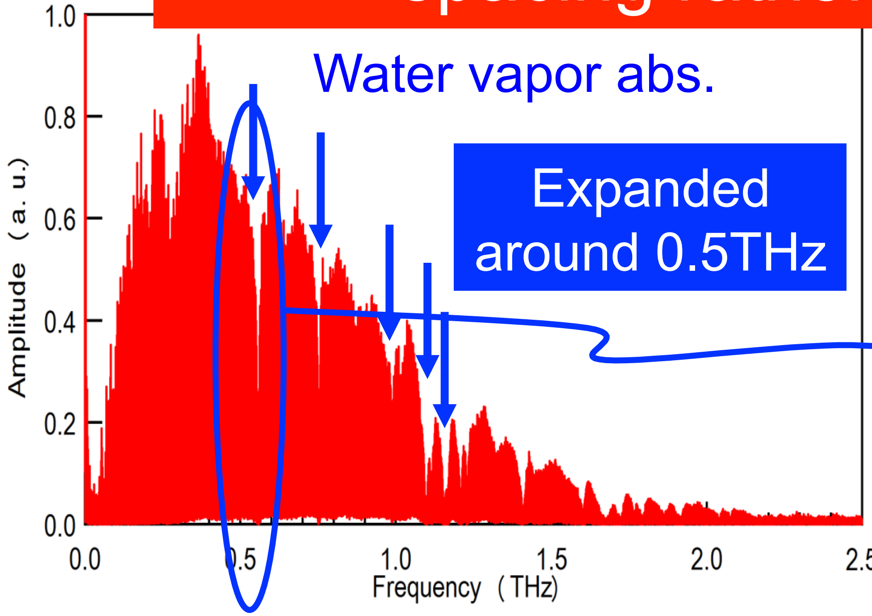
Temporal waveform

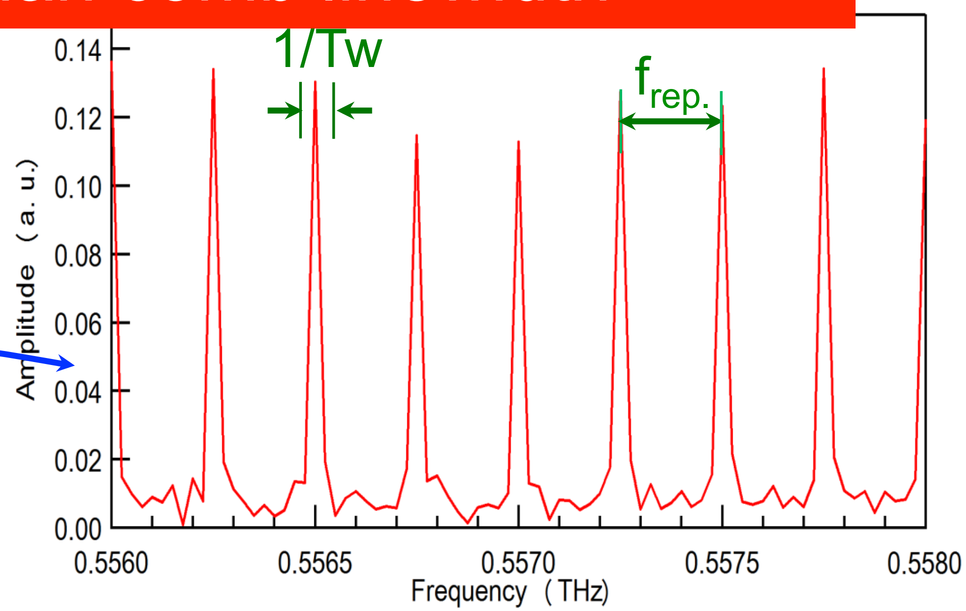


F. T.

Spectral sampling interval is limited by comb spacing rather than comb linewidth

322 (2013).





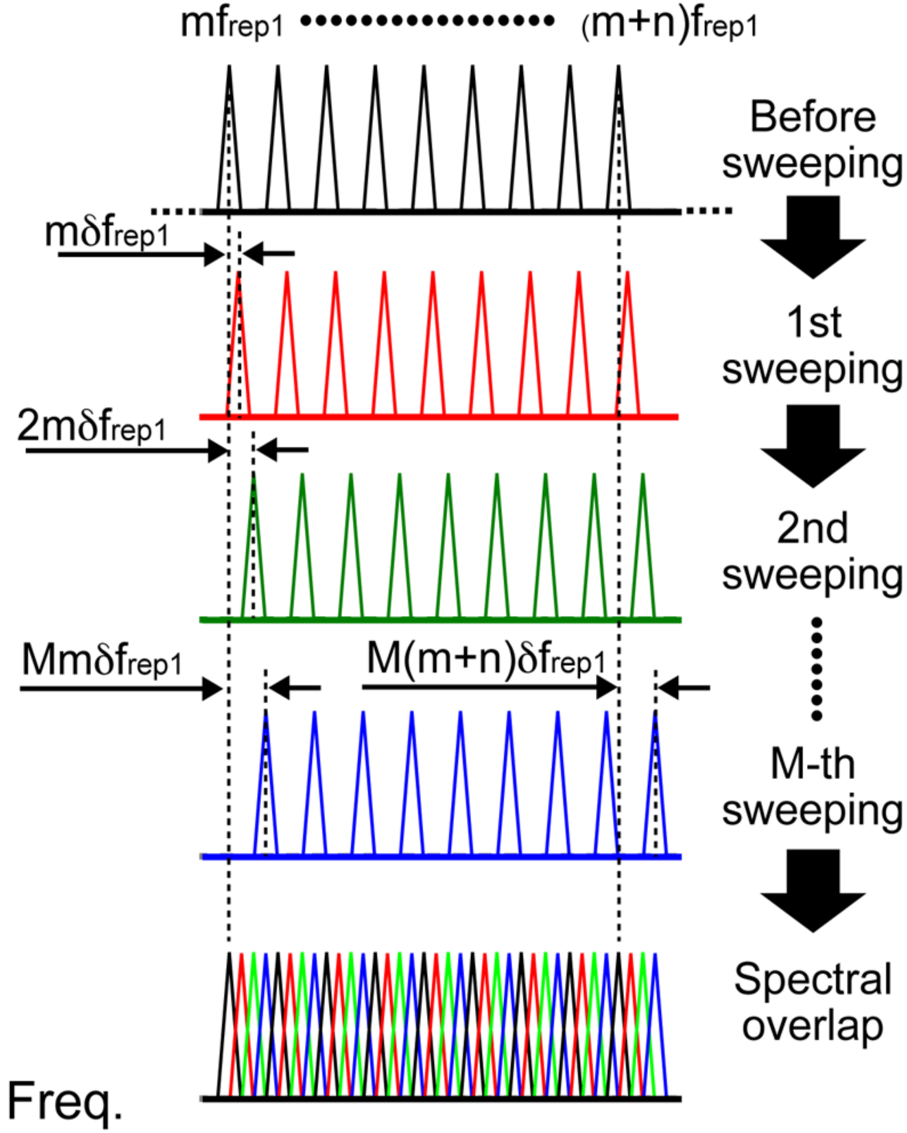
Spectrally interleaved THz comb

f_1, f_2 : tune
Δ : constant

- Sweeping at intervals of linewidth of comb mode
- Overlapping of all spectra

Gap between comb mode can be interpolated!

Equivalent to tunable CW-THz radiation



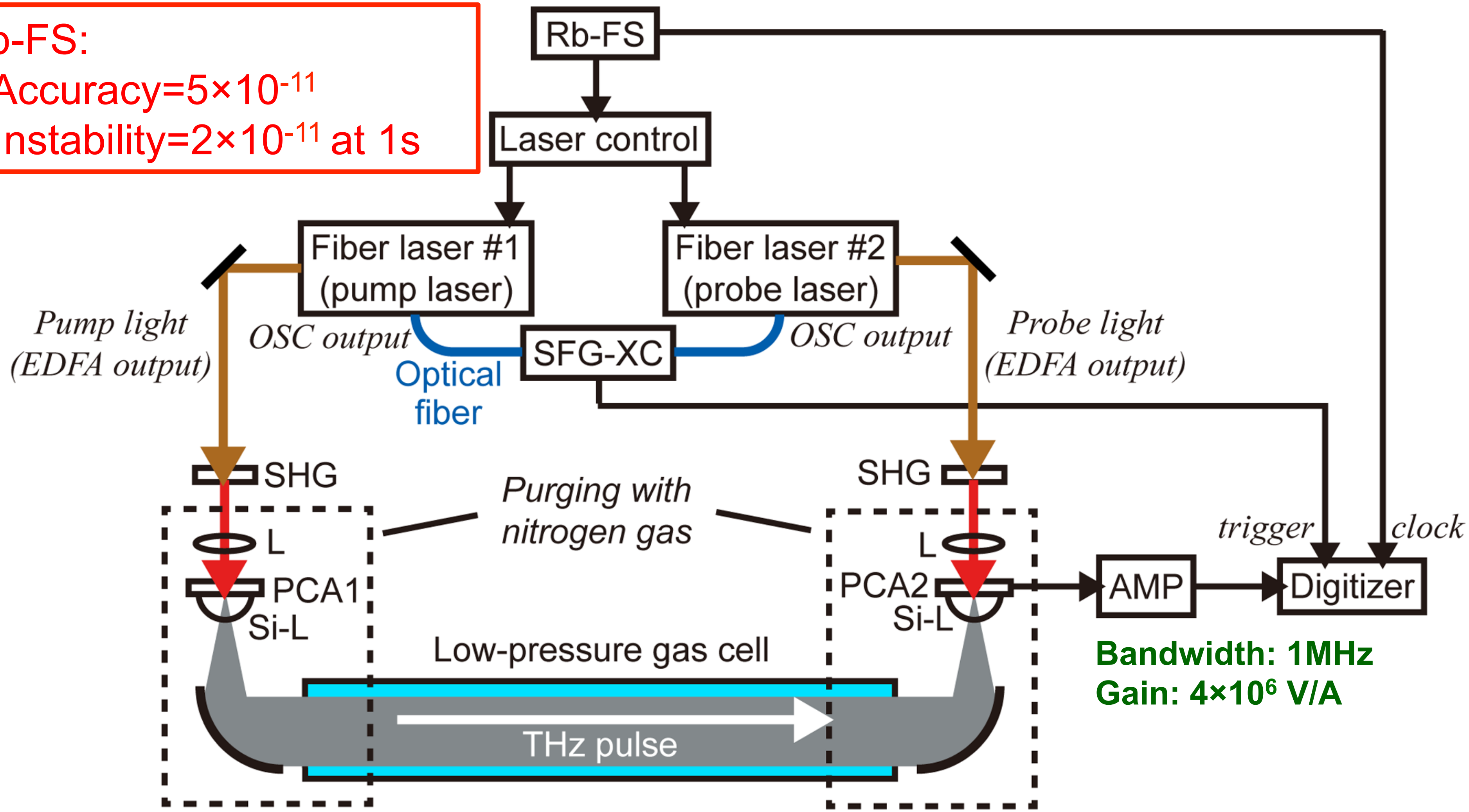
Ref) Y. -D. Hsieh, et al, Sci. Rep., **4**, 3816 (2014)

Experimental setup

λc= 1550 nm, Δt =50 fs, P_{mean}= 500mW

f_1=250,000,049Hz , f_2= 250,000,099Hz , Δf= f_2-f_1= 50Hz,

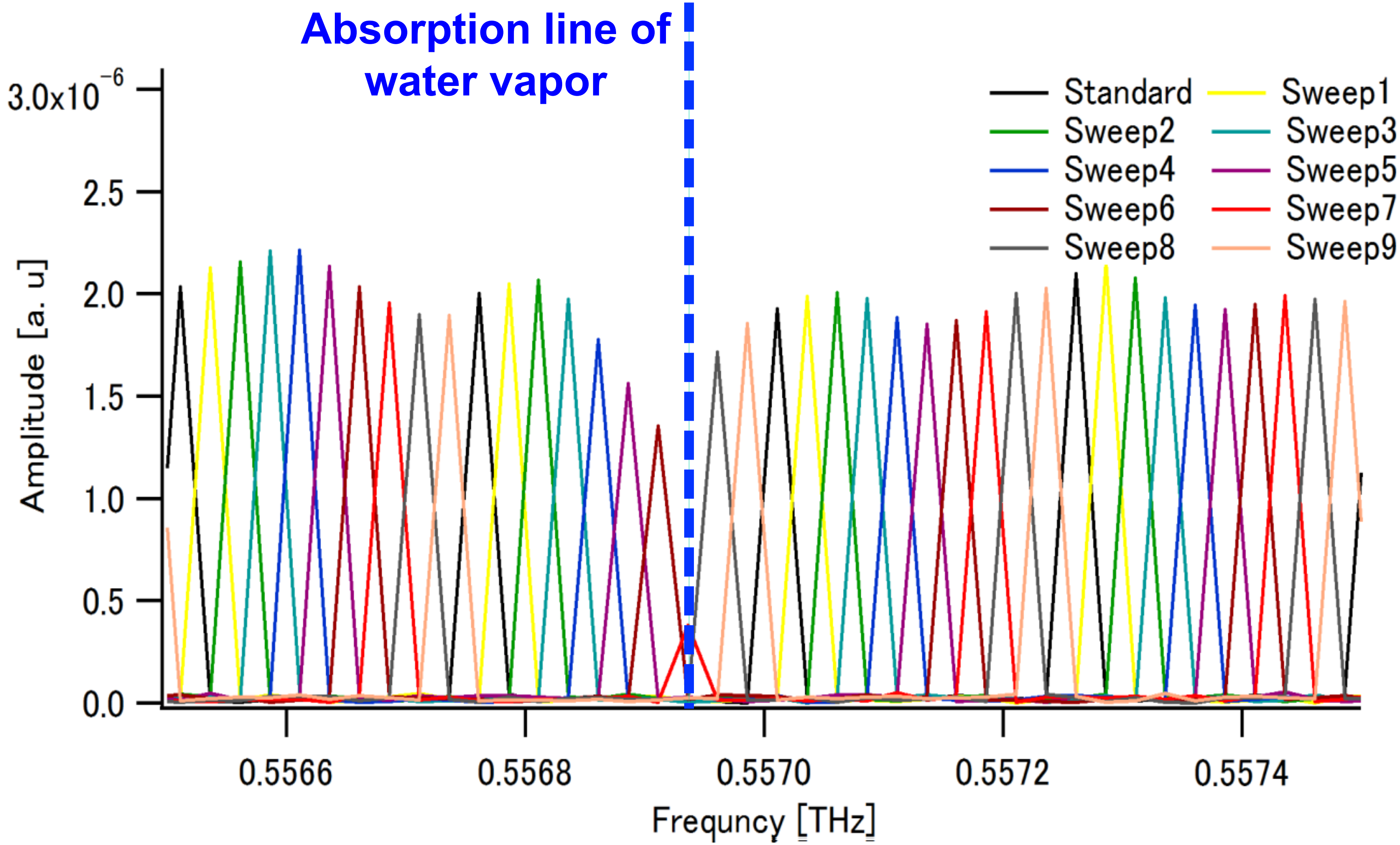
Rb-FS:
Accuracy=5×10^{-11}
Instability=2×10^{-11} at 1s



Bandwidth: 1MHz
Gain: 4×10^6 V/A

Spectroscopy of low-pressure water vapor

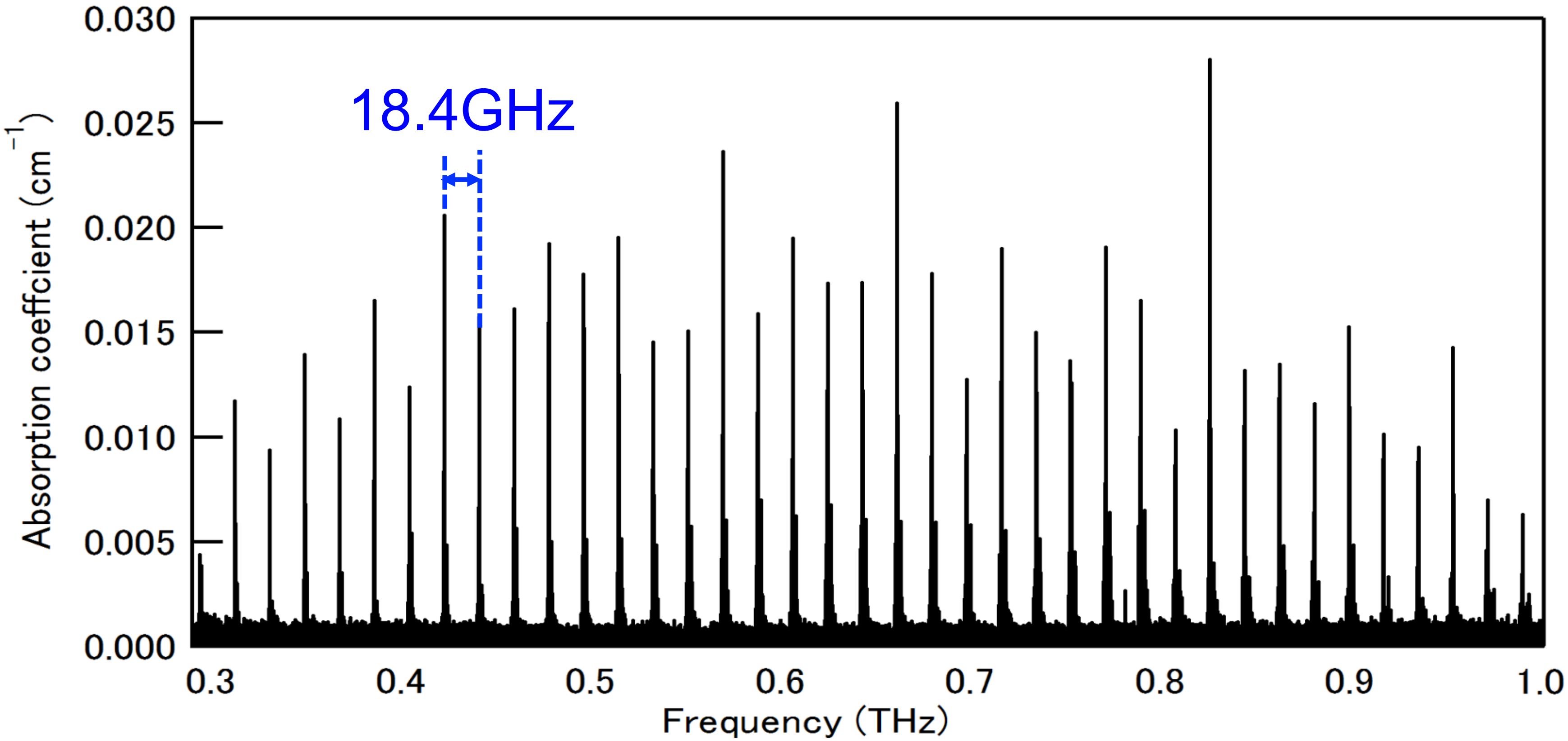
Rotational transition $1_{10} \leftarrow 1_{01}$: 0.5569360THz@NASA database
(Pressure broadening linewidth = 23 MHz @H_2O:10Pa&N_2:320Pa)



Absorbance spectrum of acetonitrile gas

- Acetonitrile (CH_3CN) :
  Symmetric top molecule, rotational constant ***B*** = 9.2 GHz
  Manifold of rotational transitions regularly spaced by 2***B***
- Total pressure: 40Pa

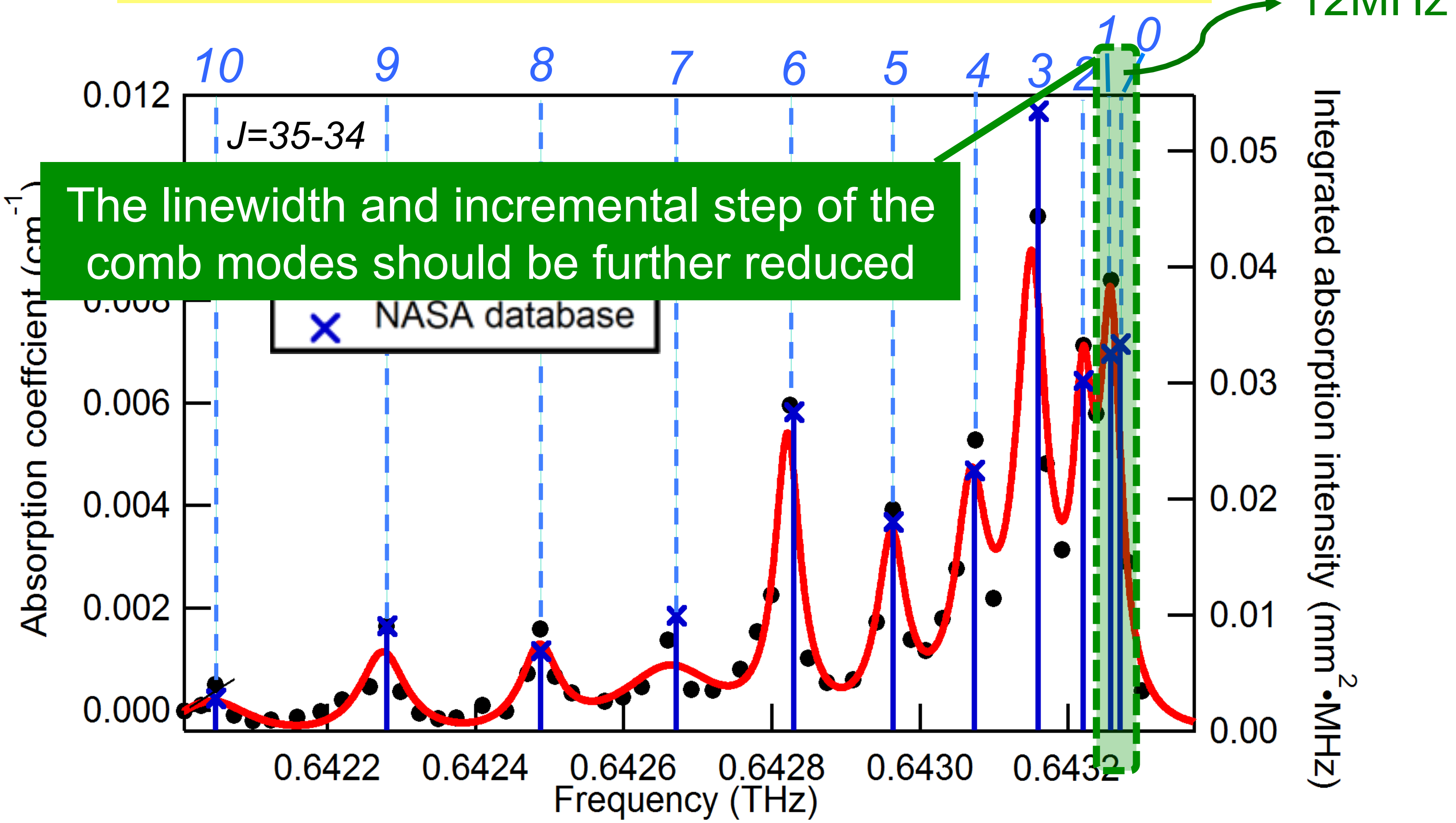
Linewidth of comb mode: 25MHz
10 times sweep



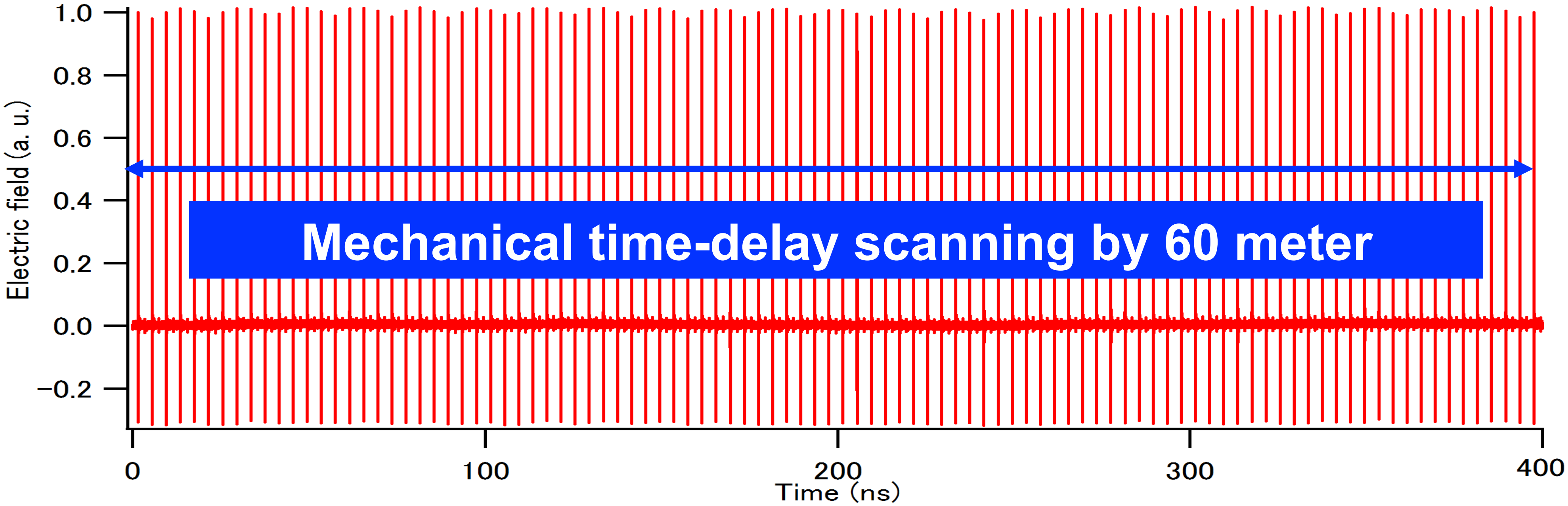
Absorbance spectrum of acetonitrile gas

Expanded around 640GHz

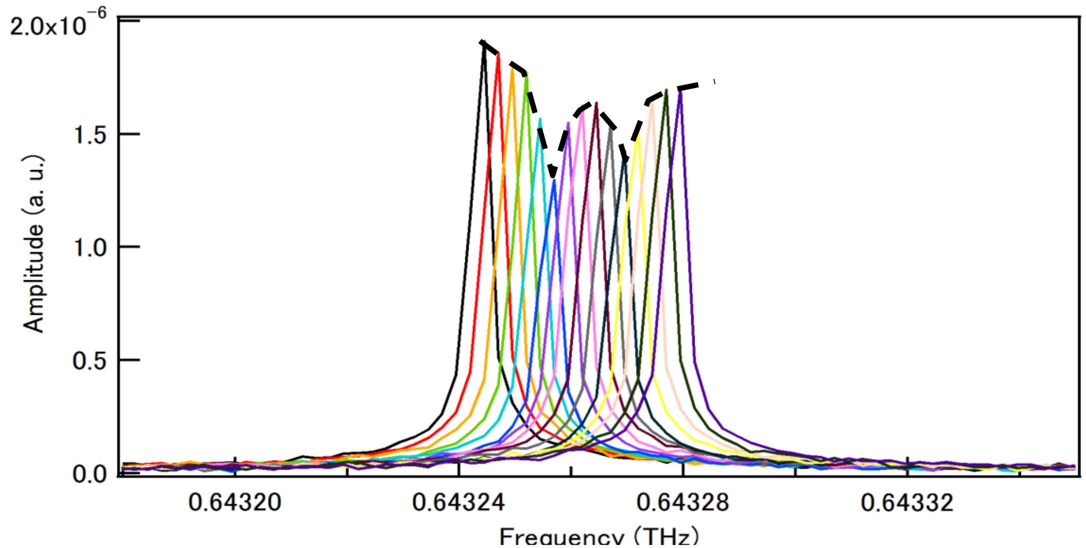
Multi-peak fitting by Lorentzian function (red line)



The linewidth and incremental step of the comb modes should be further reduced



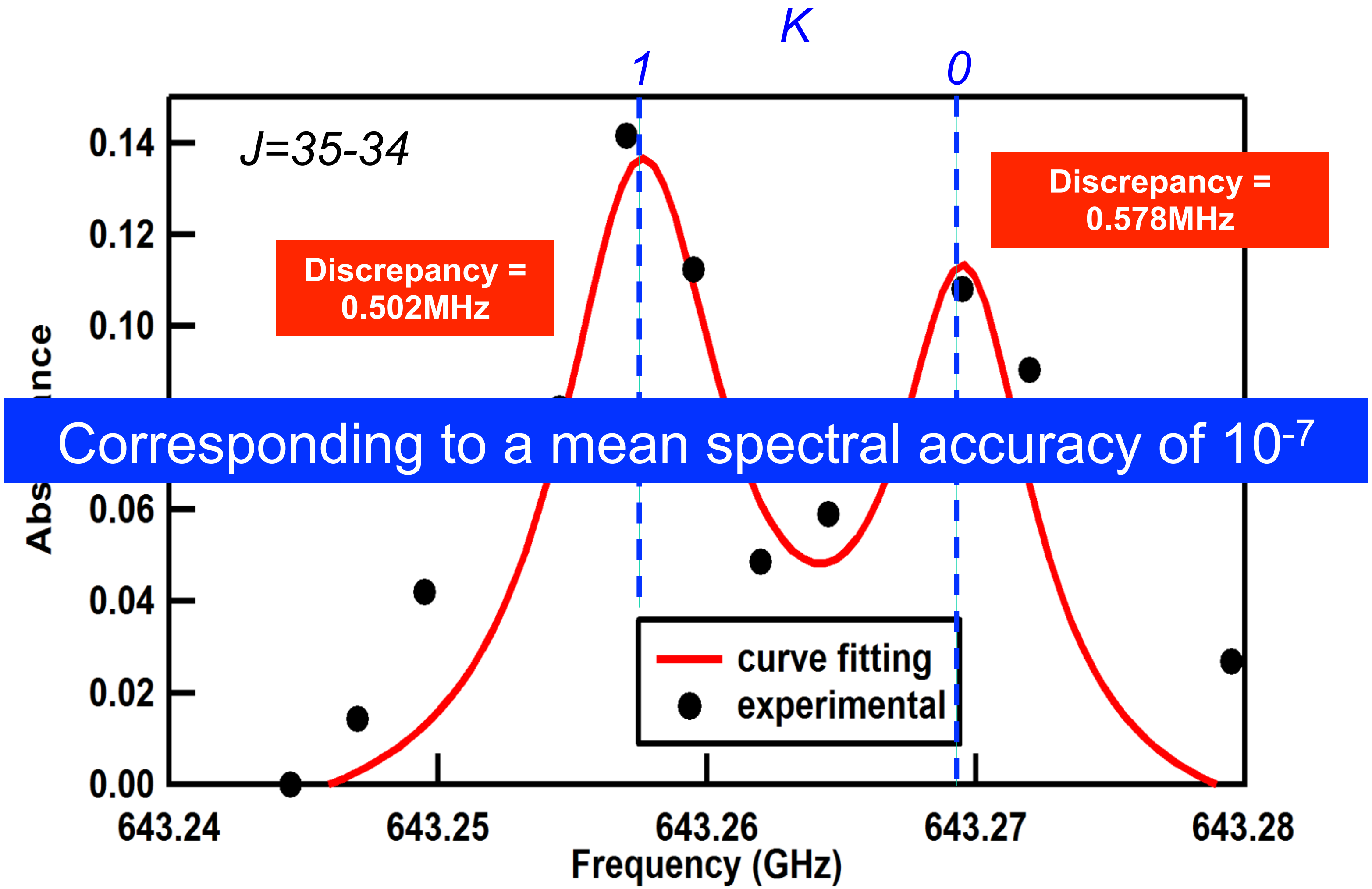
Linewidth of comb mode: 2.5MHz
15 times sweep



Absorbance spectrum of acetonitrile gas

Expended absorbance spectrum around 643GHz

Multi-peak fitting by Lorentzian function (red line)



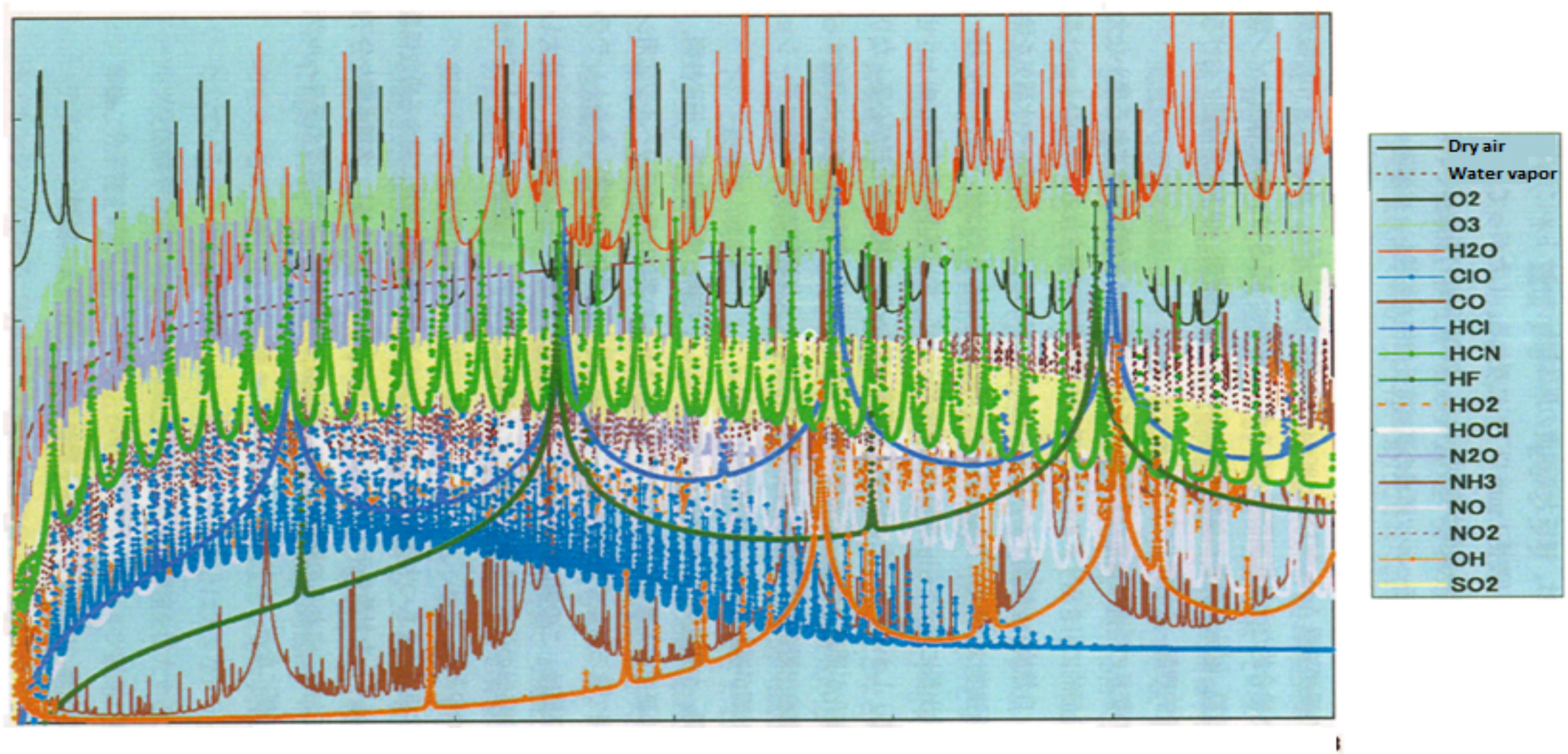
Conclusions

- Resolution = linewidth of comb mode (2.5MHz)
- Spectral accuracy: 10^{-7}
- Precise analysis of VOC gases

Future work

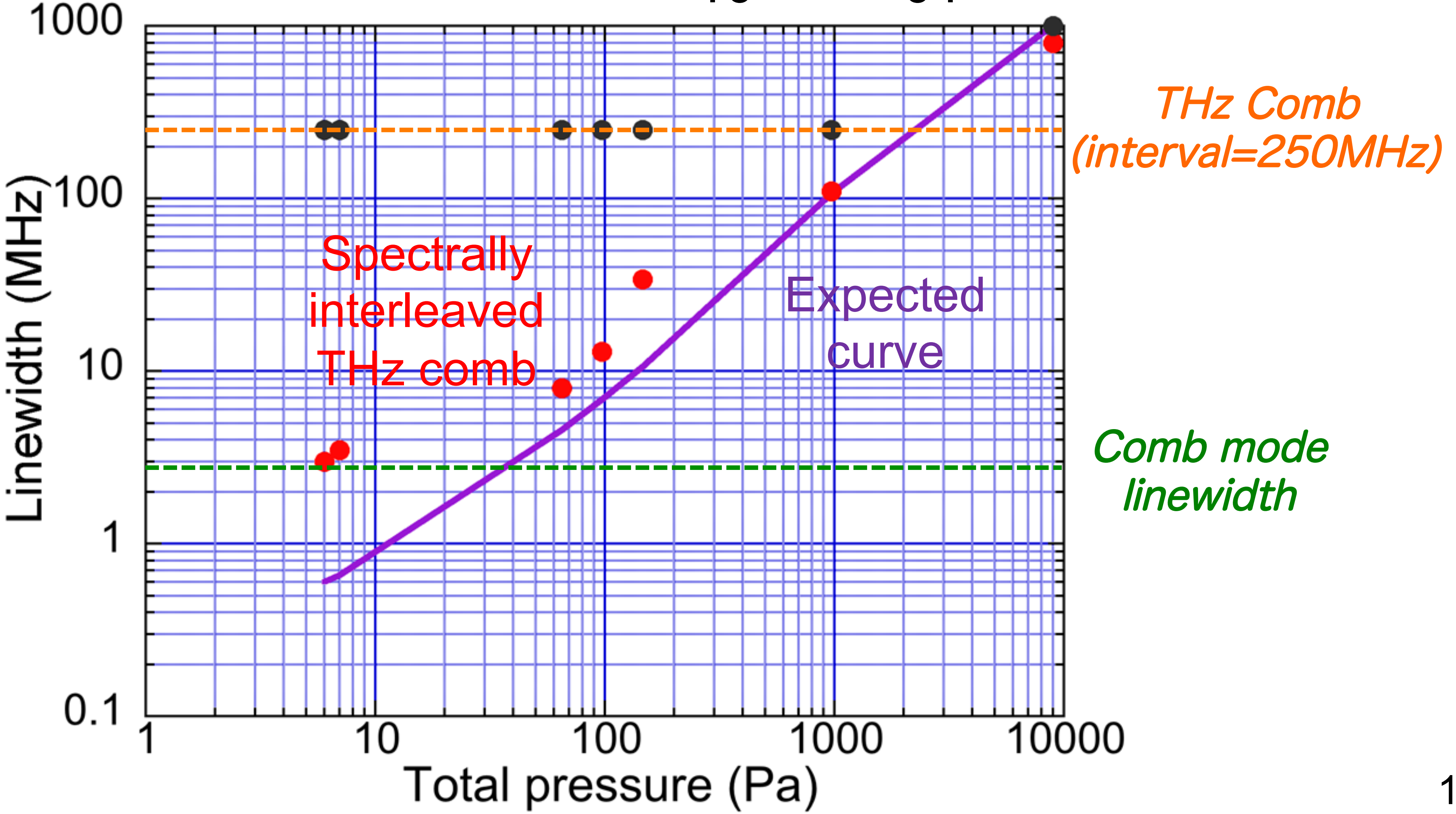
Analysis of VOC gases mixed with aerosols, smoke.

The THz spectrum of atmospheric gases



Many absorption line of atmospheric gases are concentrated in THz region

Pressure broadening characteristics of the rotational transition $1_{10} \leftarrow 1_{01}$ in water vapor



Comparison of CH_3CN absorbance peak positions with NASA database

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	<1
0	0.643269	0.643269	<1

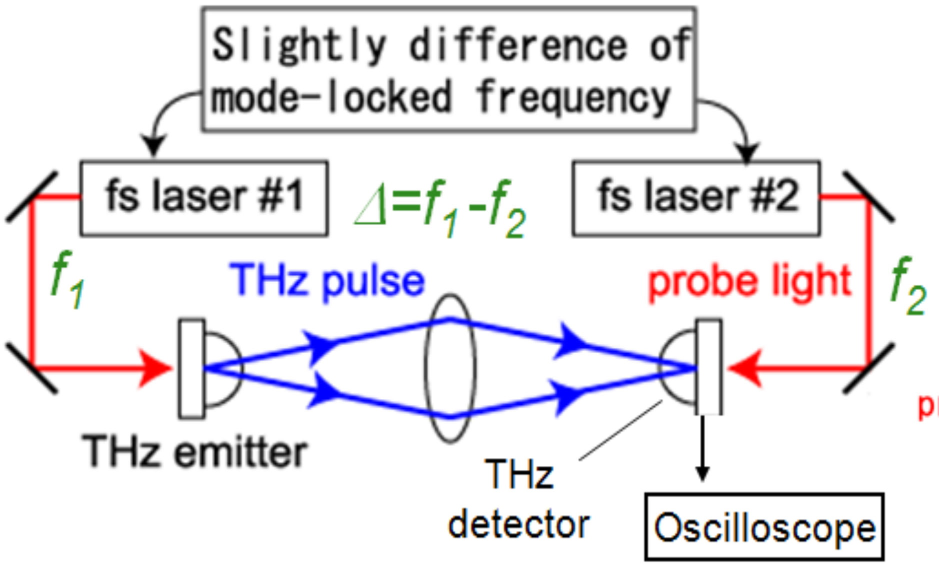
Linwidth= 25MHz

Linwidth= 2.5MHz

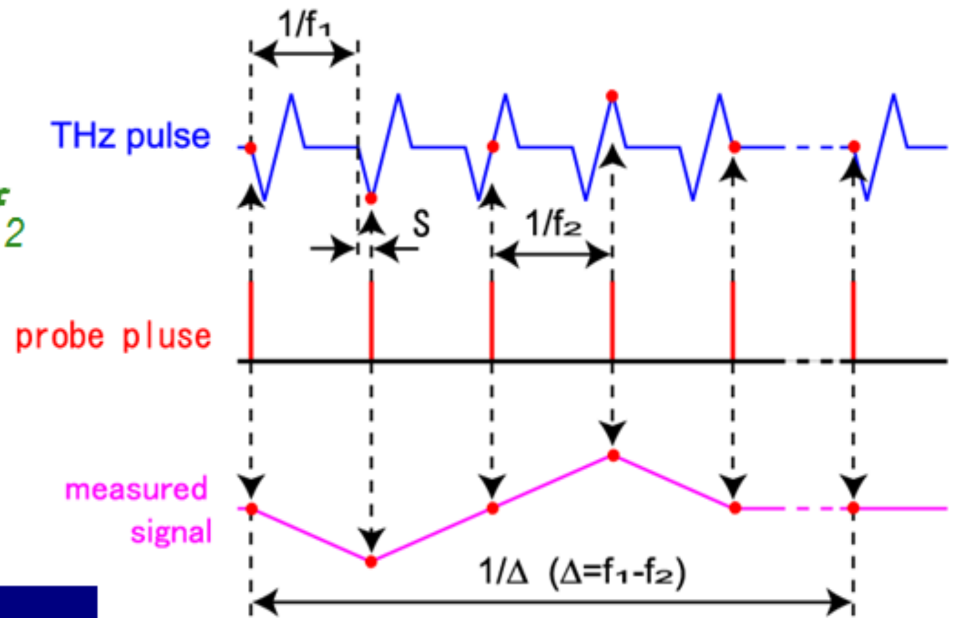
Corresponding to a mean spectral accuracy of 8.39×10^{-7}

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

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



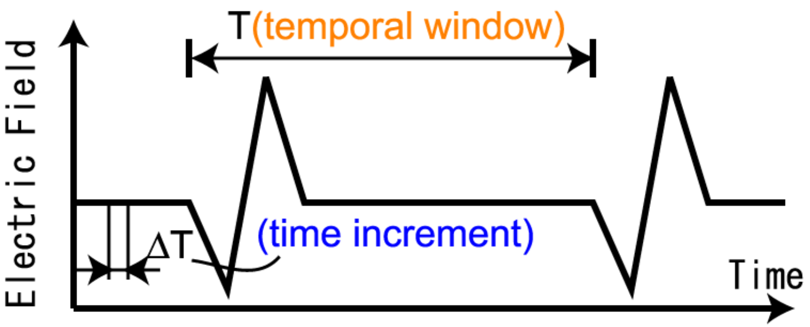
Overlap timing between THz and probe pulse is automatically shifted every pulse



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

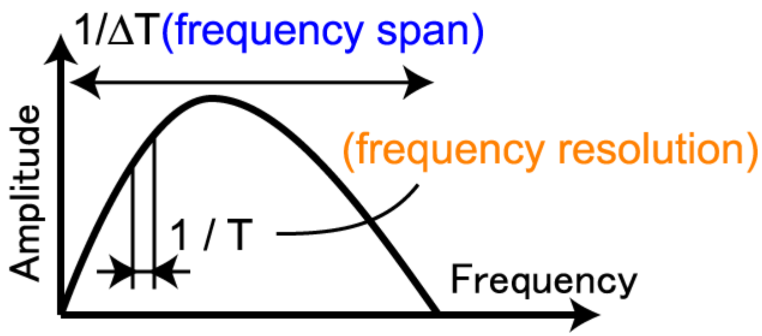
Time scale of ps THz pulse is linearly expanded to μs order

Terahertz time-domain spectroscopy



Temporal waveform

F.T.

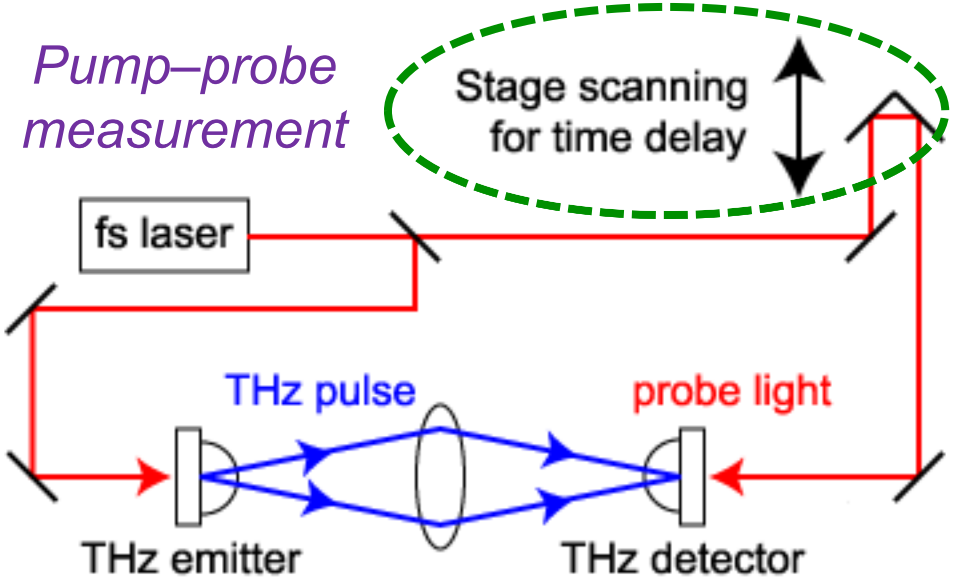


THz spectrum

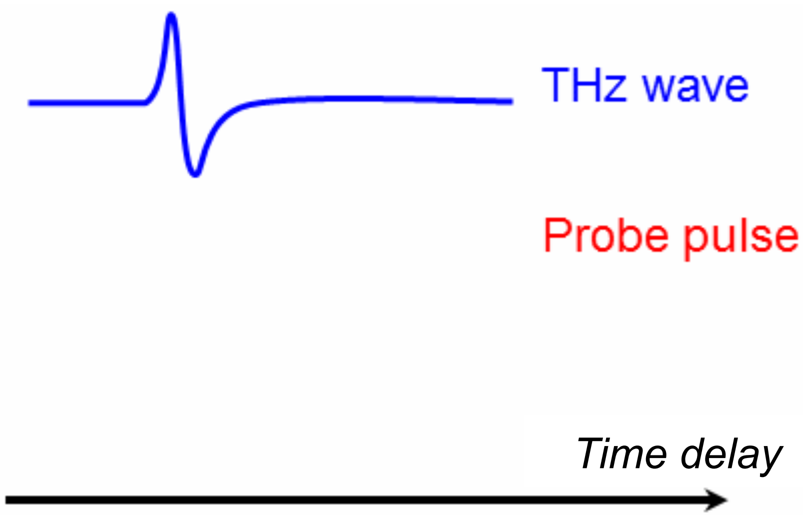
Spectral resolution = 1/Time window

Spectral accuracy Time-delay scanning

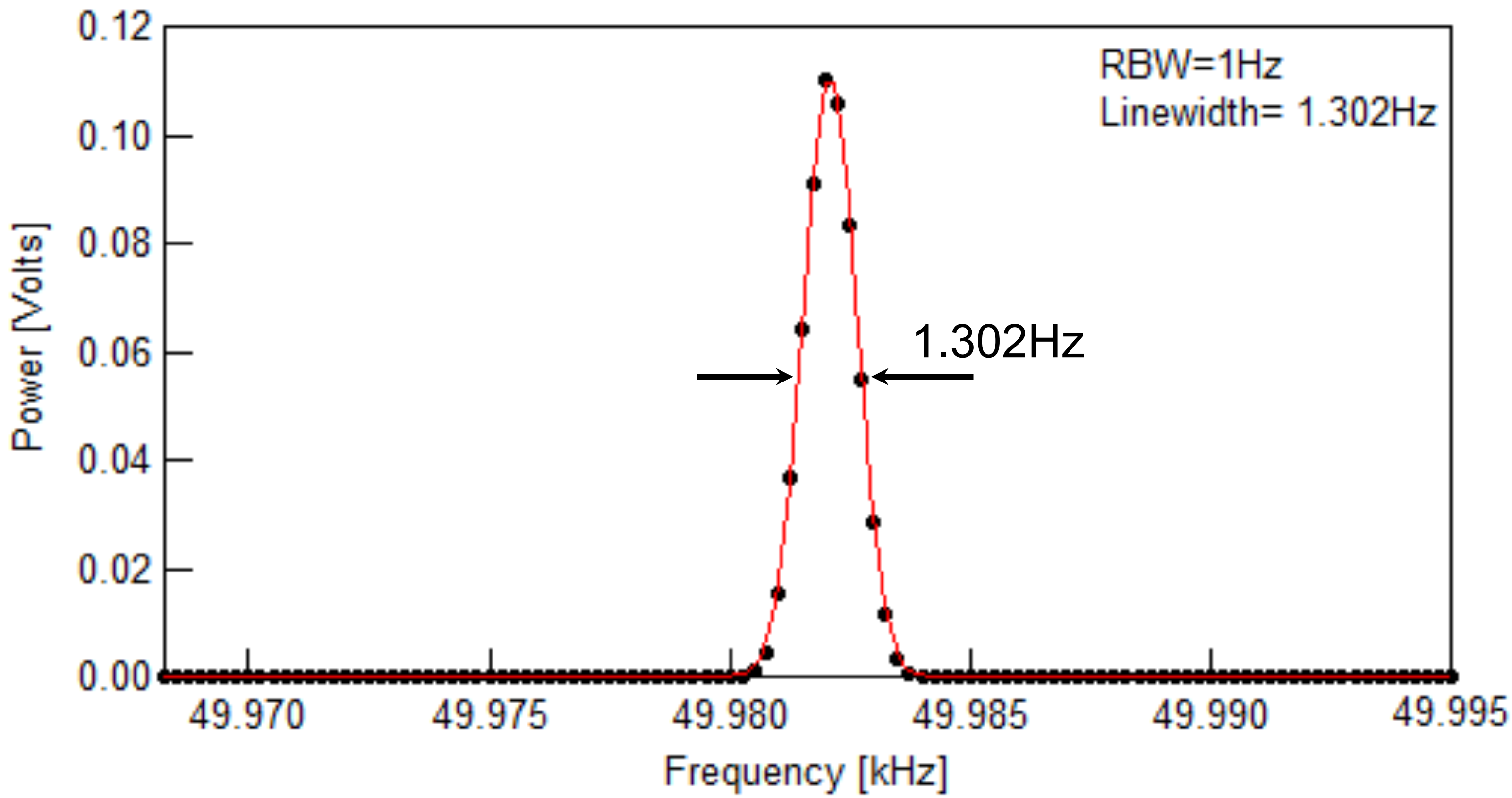
Pump–probe measurement



Determined by mechanical time delay stage

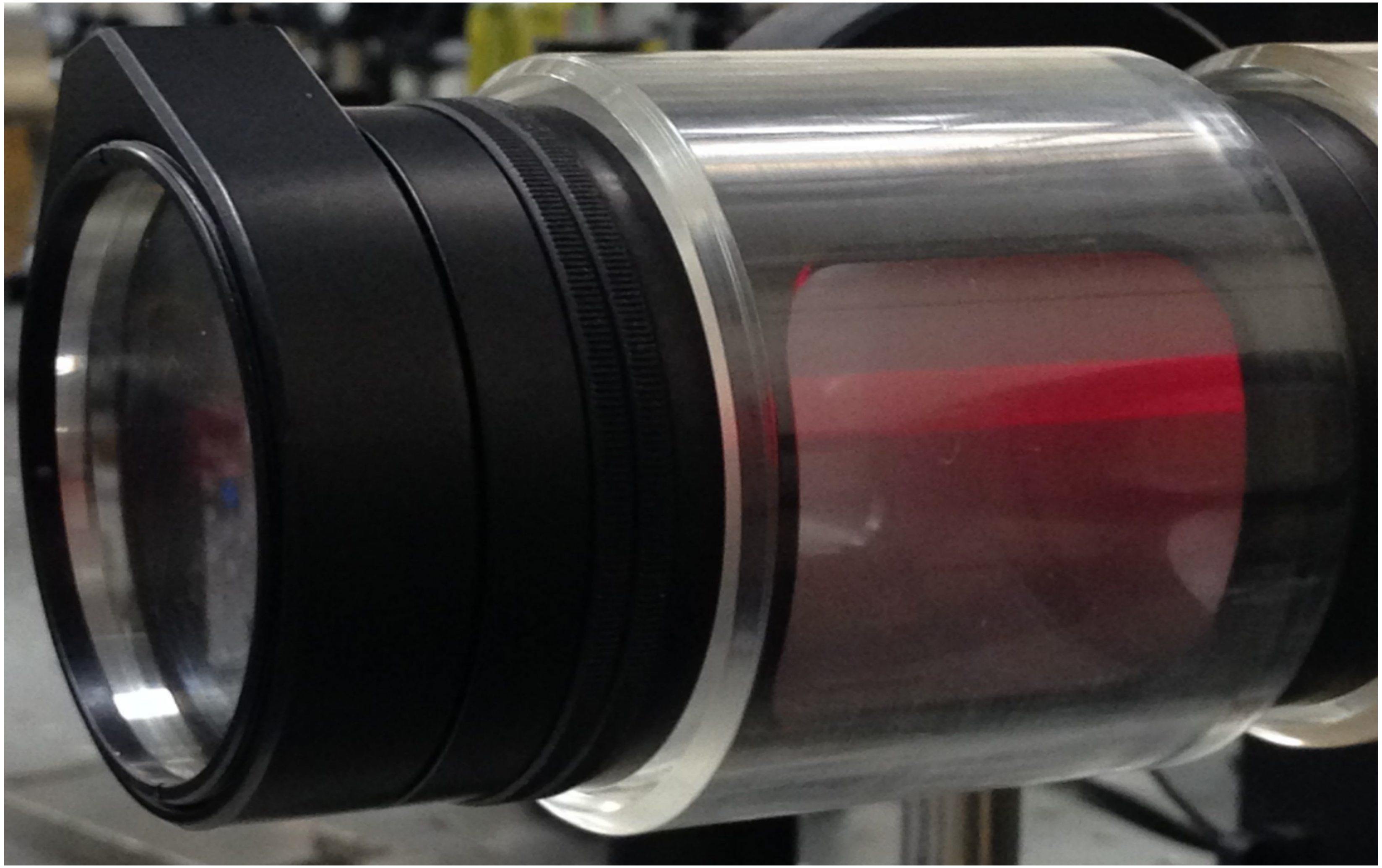


Relative linewidth of THz comb

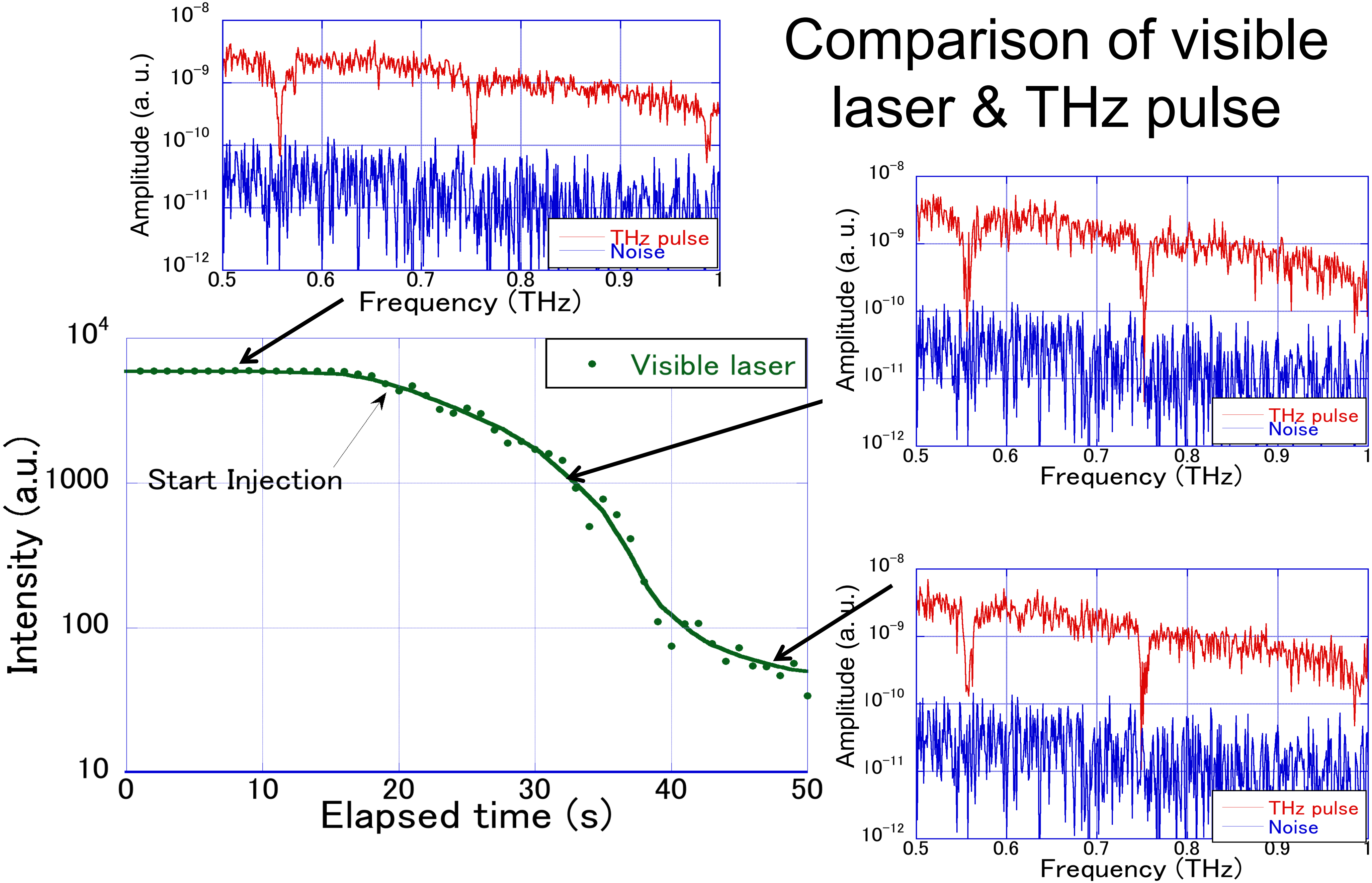


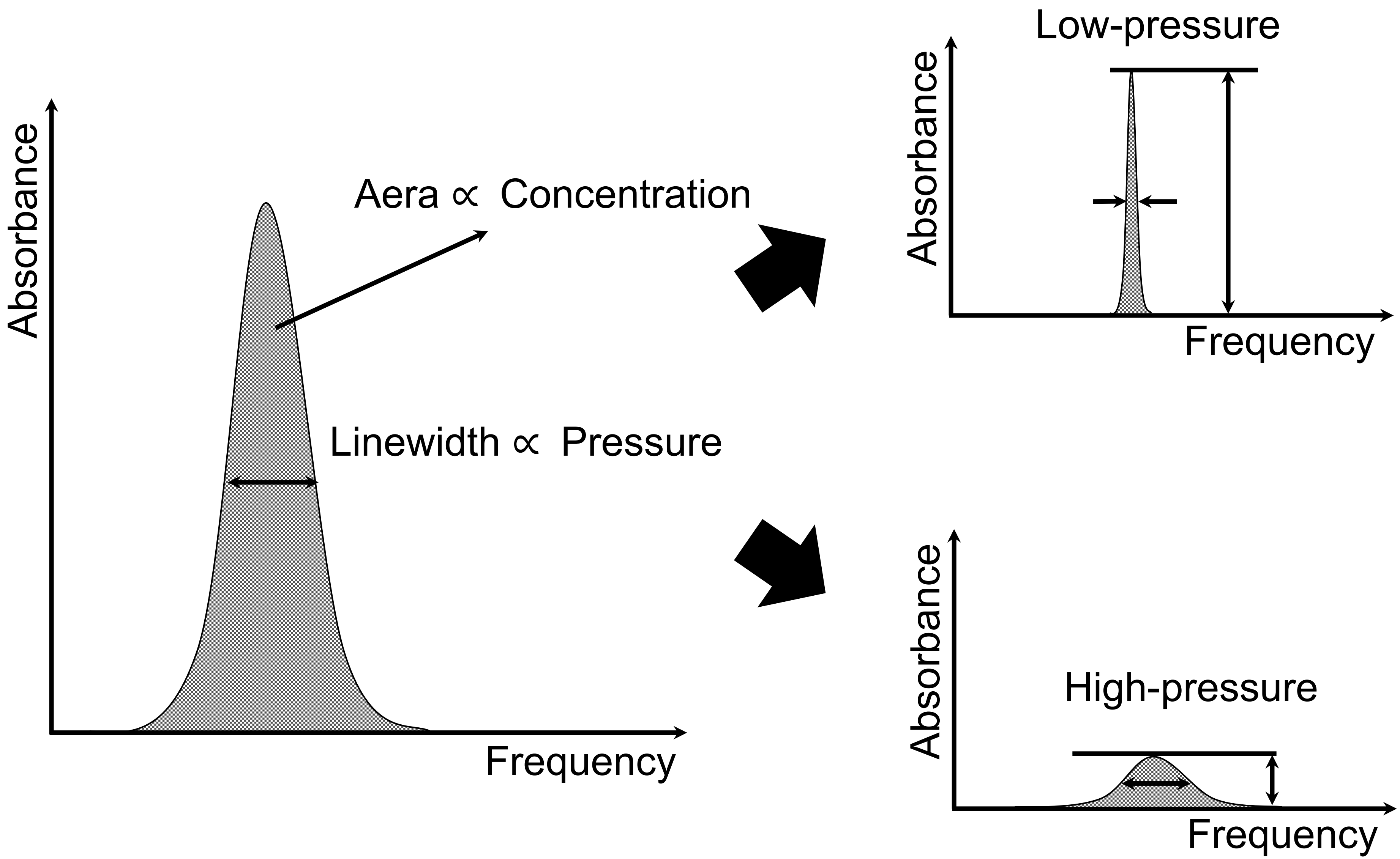
Comparison of visible laser & THz pulse

Visible laser :632nm



Comparison of visible laser & THz pulse

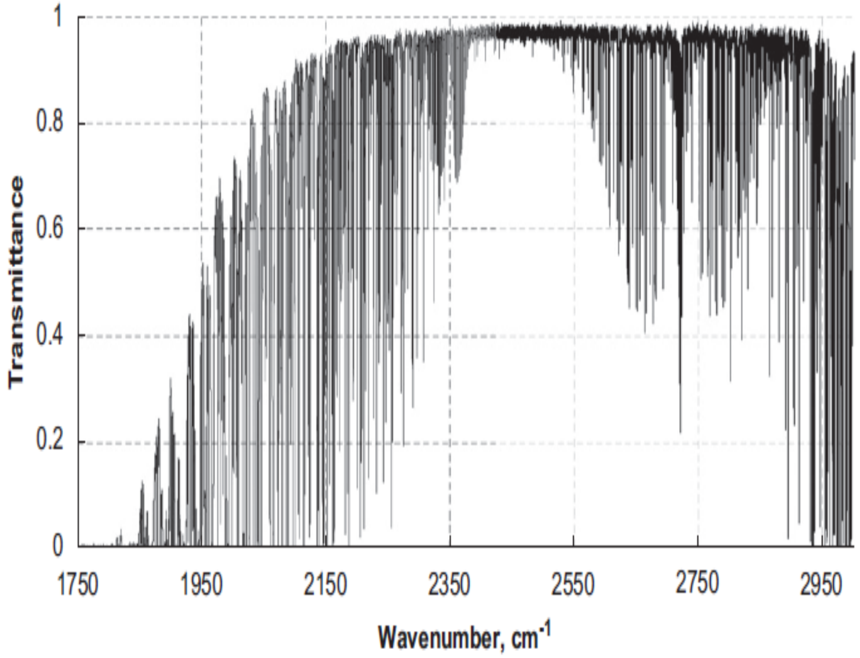


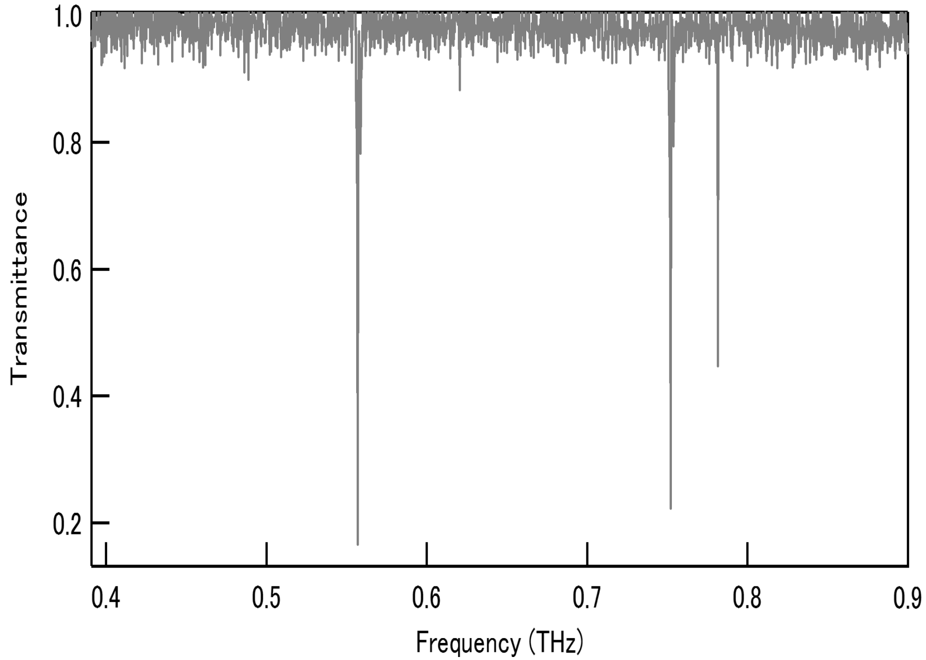

Absorbance
Frequency
Aera ∝ Concentration
Linewidth ∝ Pressure
Low-pressure
Absorbance
Frequency
High-pressure
Absorbance
Frequency

Transmittance spectrum of Water vapor

Infrared spectroscopy

THz spectroscopy





Ref) Yu. I. Baranov, et al., J. Quant. Spectrosc. Radiat. Transfer. **109**, 2291 (2008)

Doppler linewidth: $\Delta\nu = \nu/c \sqrt{2kT\ln 2/m}$