Terahertz Comb Spectroscopy Traceable to Microwave Frequency Standard

Yi-Da Hsieh, Yuki Iyonaga, Yoshiyuki Sakaguchi, Shuko Yokoyama, Hajime Inaba, Kaoru Minoshima, Francis Hindle, Yoshinori Takahashi, Masashi Yoshimura, Yusuke Mori, Tsutomu Araki, and Takeshi Yasui

Abstract—The fine-structured spectrum of a terahertz (THz) frequency comb has been observed using asynchronous-optical-sampling THz time-domain spectroscopy with an extended time window covering multiple THz pulses. Fourier transformation of 10 consecutive THz pulses enables us to obtain the spectrum of THz comb mode having a linewidth of 25 MHz at intervals of 250 MHz. Further expansion of time window up to 100 consecutive THz pulses reduces the linewidth of THz comb mode down to 2.5 MHz while conserving interval of 250 MHz. The observed THz comb mode can be used as a precise and accurate frequency marker for broadband THz spectroscopy because it is phase-locked to a microwave frequency standard by laser control. The spectroscopy of pharmaceutical tablets and low-pressure molecular gas is used to demonstrate the utility of this approach, indicating a spectral resolution of 250 MHz. The proposed method enables frequency calibration of the THz spectrometer based on a microwave frequency standard.

Index Terms—Asynchronous optical sampling, frequency comb, gas spectroscopy, Terahertz (THz) wave, THz spectroscopy.

I. INTRODUCTION

TERAHERTZ (THz) spectroscopy is appreciated as a powerful tool for sensing and material characterization due to the unique characteristics inherent in THz radiation and the abundant THz spectral fingerprints unlike from the corresponding infrared signature. The most widely used techniques in THz spectroscopy include THz time-domain spectroscopy (THz-TDS) with coherent pulsed THz radiation [1], [2], Fourier transform far-infrared spectroscopy (FT-FIR) with incoherent THz radiation [3], and THz frequency-domain spectroscopy with narrow tunable continuous-wave (CW) THz radiation (CW-THz spectroscopy). The last method can be further classified into photonic [4] and electronic [5] based systems depending on the source and detector. Both THz-TDS and FT-FIR have the merit of providing a broad spectral coverage but suffer from poor spectral resolution owing to mechanical time-delay scanning. Furthermore, since the frequency scale in THz spectrum obtained by these methods is not assured by a frequency standard, there is a possibility that the spectrum of a sample is not necessarily the same among different apparatuses. In the case of the photonic-based CW-THz spectroscopy, high spectral resolution can be achieved but the accessible spectral range is usually narrower than that of THz-TDS and FT-FIR. Furthermore, the mode hopping of the CW-THz radiation often limits the continuous tuning when a broad spectral range is required. On the other hand, the electronic-based system provides fast sweeping of high spectral purity without mode hopping, high brightness sources, and exact frequency determination with electronic frequency reference to CW-THz spectroscopy. However, the accessible spectral range is still limited to a few hundreds GHz. In this way, each of these methods has its merits and weaknesses. If one could combine the merits of them, it would be possible to further expand the application field of THz science and technology based on high performance and reliable frequency metrology.

Recently, THz frequency combs have started to reveal their potential for THz frequency metrology [6], such as spectroscopy [7], [8], frequency measurement [9]–[12], and signal generation [13]–[15]. A THz comb, which is a description of pulsed THz radiation in the frequency domain, is composed of a series of CW-THz waves regularly separated by the mode-locked frequency of the pulsed THz radiation. In the case of frequency metrology a THz comb is attractive due to the narrow-linewidth of the CW-THz waves that provide regular frequency marks over a wide spectral band. Furthermore, the absolute frequencies of all comb modes can be phase-locked to a microwave frequency standard by laser control. These characteristics enable us to use a THz comb as a precise ruler of THz frequency. For example, THz-comb-referenced spectrum analyzer has been successively applied to the measurement of absolute frequency in CW-THz sources with an accuracy of 10^{-11} to 10^{-13} [9]–[12]. Furthermore, the THz comb should combine the merits of both THz-TDS and CW-THz

Y.-D. Hsieh, Y. Iyonaga, Y. Sakaguchi, and T. Araki are with the Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan (e-mail: sya@sml.me.es.osaka-u.ac.jp; iyonaga@sml.me.es.osaka-u.ac.jp; sakaguti@me.es.osaka-u.ac.jp; araki@me.es.osaka-u.ac.jp).

S. Yokoyama is with the Micro Optics Company, Ltd., Nishikyo, Kyoto 610-1104, Japan (e-mail: shuko.yokoyama@micro-optics.jp).

H. Inaba and K. Minoshima are with the National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8563, Japan (e-mail: h.inaba@aist.go.jp; k.minoshima@aist.go.jp).

F. Hindle is with the Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque 59140, France (e-mail: francis.hindle@univ-littoral.fr).

Y. Takahashi, M. Yoshimura, and Y. Mori are with the Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan (e-mail: takahashi@cryst.eei.eng.osaka-u.ac.jp; yoshi@eei.eng.osaka-u.ac.jp; mori.yusuke@eei.eng.osaka-u.ac.jp).

T. Yasui is with the Institute of Technology and Science, The University of Tokushima, Tokushima, Tokushima 770-8506, Japan (e-mail: yasui.takeshi@tokushima-u.ac.jp).

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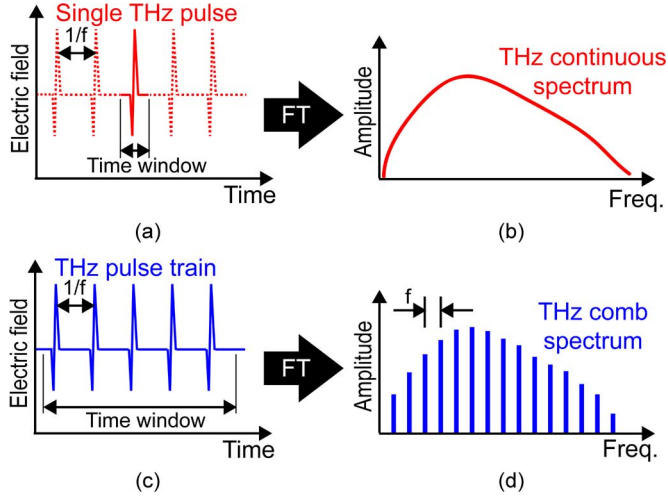Digital Object Identifier 10.1109/TTHZ.2013.2250333

Fig. 1. (a) Temporal waveform of single THz pulse and (b) corresponding THz continuous spectrum. (c) Temporal waveform of THz pulse train and (d) corresponding THz comb spectrum.
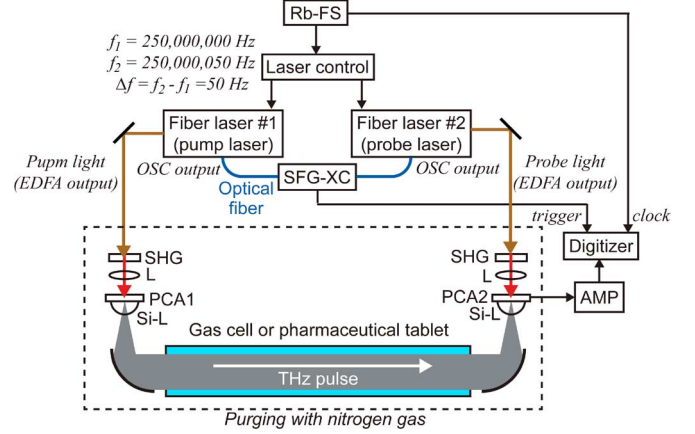

Fig. 2. Experimental setup. Rb-FS: rubidium frequency standard; SFG-XC: sum-frequency-generation cross-correlator; SHGs: second-harmonic-generation crystals; Ls:lenses; EDFA: erbium-doped fiber amplifier; OSC, erbium-doped fiber oscillator; PCA1: dipole-shaped LT-GaAs photoconductive antenna for THz generation; PCA2: dipole-shaped LT-GaAs photoconductive antenna for THz detector; Si-Ls: silicon lenses; AMP: current preamplifier.

spectrometers, so that it can show the frequency scale of the spectrum based on a frequency standard. There are some studies that report the observation of detailed spectrum of THz comb itself based on the multi-frequency-heterodyning technique [7], [8]; however, poor signal-to-noise ratio (SNR) in spectral amplitude, arising from frequency-domain measurement with a spectrum analyzer, hinders the application of THz comb to practical spectroscopy. In this paper, an SNR-enhanced THz comb spectrum is obtained by the use of time-window-extended asynchronous-optical-sampling THz-TDS (ASOPS-THz-TDS). Furthermore, the THz spectroscopy of several samples using a THz comb is demonstrated.

II. TIME-WINDOW-EXTENDED ASOPS-THZ-TDS

Here, let us consider how we can acquire the fine-structured spectrum of a THz comb, which surpasses spectral resolution of conventional THz spectroscopy. A traditional THz-TDS system employing mechanical time-delay scanning usually measures the temporal waveform of only a single THz pulse, as shown in Fig. 1(a). Taking the Fourier transformation (FT) of the waveform gives the continuous spectrum of the broadband THz radiation without comb structure, as shown in Fig. 1(b). On the other hand, if the time window is greatly expanded to cover more than one pulse period, one can measure the temporal waveform of consecutive THz pulses, that is to say, a THz pulse train, as shown in Fig. 1(c). Taking the FT of this will give the fine-structured spectrum of the THz comb because FT of the periodic THz pulses imprints a frequency modulation on THz spectrum, as shown in Fig. 1(d).

However, in conventional THz-TDS system it is not practical to measure such a temporal waveform of THz pulse train because it requires scanning over a long time delay. Instead, we focus on ASOPS-THz-TDS using two mode-locked lasers with slightly mismatched mode-locked frequencies [8], [16]–[19]. Since ASOPS-THz-TDS enables us to expand ps time scale of THz pulse up to the μs scale based on the principle of asynchronous optical sampling [20], the resulting slow temporal waveform can be directly measured by a standard oscilloscope without the need for the mechanical time-delay scanning. One

can, therefore, arbitrarily adjust the observed time window of THz pulse temporal waveform by changing the time scale of the oscilloscope. Conventionally, the ASOPS-THz-TDS has been used to acquire the temporal waveform of the single THz pulse within the range of the time window equal to one pulse period; however, it is possible to extend the time window to more than one pulse period due to its non-mechanical nature of the time-delay scanning.

III. EXPERIMENTAL SETUP

Our ASOPS-THz-TDS system consists of dual mode-locked Er-fiber lasers (ASOPS TWIN 250 with P250, Menlo Systems; center wavelength = 1550 nm, pulse duration = 50 fs, mean power = 500 mW) and a delay-stage-free THz-TDS setup including a pair of photoconductive antenna (PCA) as shown in Fig. 2. The individual mode-locked frequencies of the two lasers (f_1 = 250 000 000 Hz and f_2 = 250 000 050 Hz) and the frequency offset between them ($\Delta f = f_2 - f_1 = 50$ Hz) were stabilized by two independent laser control systems referenced to a rubidium frequency standard (Rb-FS, accuracy = 5×10^{-11} and instability = 2×10^{-11} at 1 s). After wavelength conversion of the two laser beams by second-harmonic-generation crystals (SHGs), pulsed THz radiation was emitted by a dipole-shaped, low-temperature-grown, GaAs PCA (LT-GaAs-PCA) triggered by pump light (PCA1; pump power = 18 mW, bias voltage = 20 V), and was then detected by another dipole-shaped LT-GaAs-PCA triggered by probe light (PCA2; probe power = 9 mW). The optical path in which the THz beam propagated was purged with dry nitrogen gas to avoid absorption by atmospheric moisture. Portions of the output light from the two lasers were fed into a sum-frequency-generation cross-correlator (SFG-XC). The resulting SFG signal was used to generate a time origin signal in the ASOPS-THz-TDS. After amplification with a current preamplifier (AMP, bandwidth = 1 MHz, gain = 4×10^6 V/A), the temporal waveform of the output signal from PCA2 was acquired with a digitizer (sampling rate = 2 MS/s, resolution = 20 bit) by using

the SFG-XC signal as a trigger signal. Then, time scale of the observed signal was calibrated by a temporal magnification factor of $f_1/\Delta f (= 250\,000\,000/50 = 5\,000\,000)$ [17]. Finally, the amplitude spectrum of THz comb was obtained by FT of the temporal waveform of THz pulse train.

IV. RESULTS

A. Basic Performance

To acquire the temporal waveform of 10 consecutive THz pulses, we set the time window of the digitizer to 10 pulse periods$(= 0.2\ s)$ with a sampling rate of 2 MS/s and 400 000 samples per acquisition. Once the SFG signal triggered the measurement of the temporal waveform, the data acquisition was continued until the completion of the 400 000 samples. During this data acquisition period, any SFG signal was disregarded and was not treated as a trigger signal. As a result, the temporal waveform with the time window size of 40 ns was measured. Since this temporal waveform was composed of 400 000 samples, the real time sampling interval is 100 fs.

Fig. 3(a) shows the acquired temporal waveform of the THz pulse train, obtained by repeating the measurement of the temporal waveform over 10 consecutive THz pulses (acquisition time for single sweep $= 0.2\ s$) 5000 times and integrating the data (integration number $= 5000$, acquisition time $= 1000\ s$). Ten consecutive THz pulses are clearly observed at an interval of 4 ns. Also, the peak-to-peak value in electric filed has no deviation for these THz pulses, implying negligible influence of the timing jitter. Actually, 10 repetitive measurements of the temporal waveform without signal integration indicated that the accumulated timing jitter was 105 fs for the tenth THz pulse in Fig. 3(a). Small modulation observed in the interval of the THz pulses is mainly due to electromagnetic noise propagating in free space.

Fig. 3(b) shows a magnified temporal waveform of the first THz pulse. The transient evolution of the pulsed THz radiation in the picosecond region was also observed clearly. A dynamic range of time scale DR_{time} in this measurement is calculated as follows:

$$DR_{time} = 20 \log \left(\frac{\text{time window}}{\text{sampling step of time}} \right)$$
$$= 20 \log \left(\frac{40 \times 10^{-9}}{100 \times 10^{-15}} \right) = 112 \text{ dB}. \quad (1)$$

Such a wide DR_{time} leads to wide dynamic range of frequency scale that can resolve fine-structured spectrum of the broad THz comb although the actual spectral range depends on the performance of THz emitter and detector and/or timing jitter between the dual fiber lasers.

The red line in Fig. 3(c) shows the amplitude spectrum of the THz comb obtained by taking the FT of the temporal waveform of the THz pulse train in Fig. 3(a). In contrast, the blue line in Fig. 3(c) shows a continuous spectrum of the THz amplitude obtained by taking the FT of the temporal waveform of the single THz pulse (time window $= 4\ ns$) measured with one-pulse-period ASOPS-THz-TDS [19]. The spectral envelop of the THz comb spectrum is in good agreement with the spectral shape of the THz continuous spectrum. This indicates that our ASOPS-THz-TDS can capture the temporal waveform of
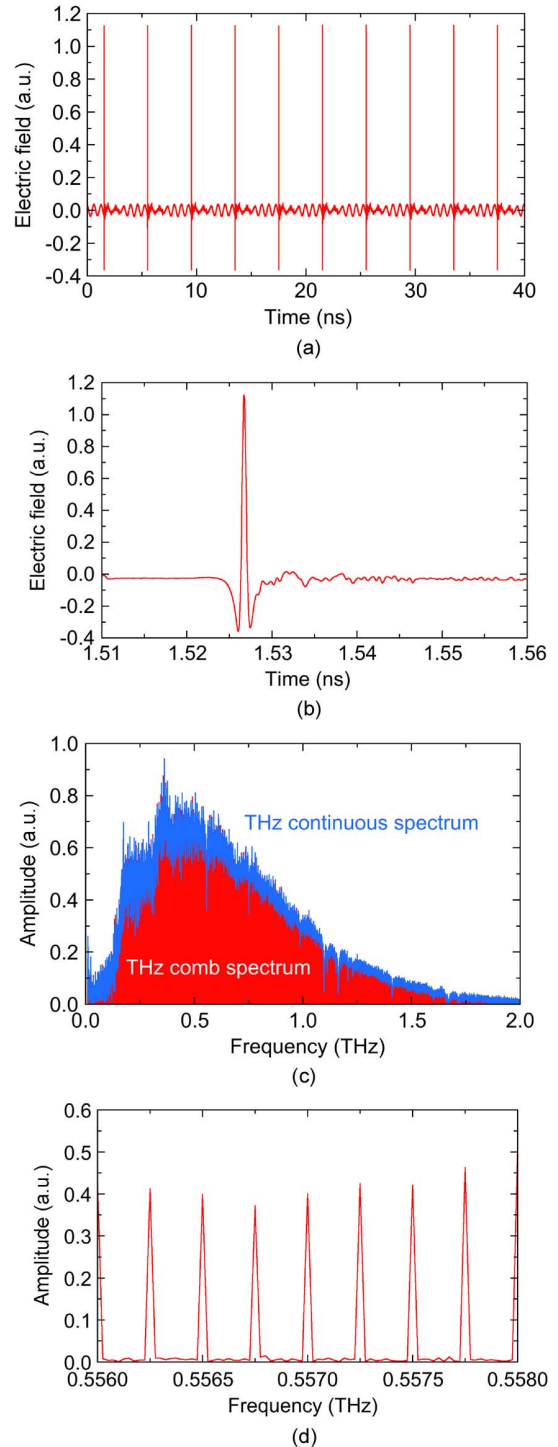

Fig. 3. Temporal waveform of electric field in: (a) 10 consecutive THz pulses (time window $= 40$ ns) and (b) the first THz pulse (time window $= 50$ ps). (c) Comparison of amplitude spectrum between THz comb spectrum and THz continuous spectrum. (d) Amplitude spectrum of THz comb mode around 0.557 THz.

THz pulse train correctly without influence of timing jitter between dual fiber lasers and/or pulse-to-pulse timing jitter.

The spectrum of THz comb is composed of a series of frequency spikes regularly separated by the mode-locked frequency of the laser. To observe its detailed structure, we expanded the spectral region around 0.5570 THz, as shown in
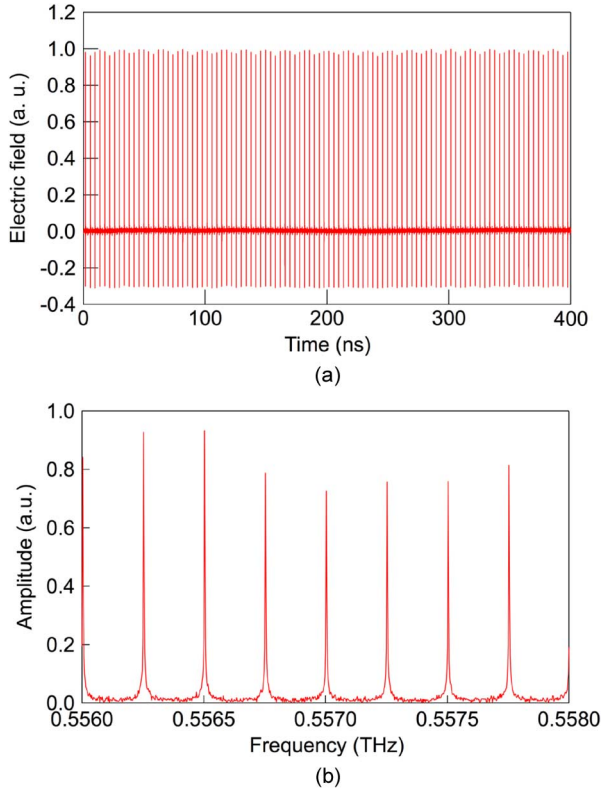
Fig. 4. (a) Temporal waveform of electric field in 100 consecutive THz pulses (time window = 400 ns). (b) Amplitude spectrum of THz comb mode around 0.557 THz.
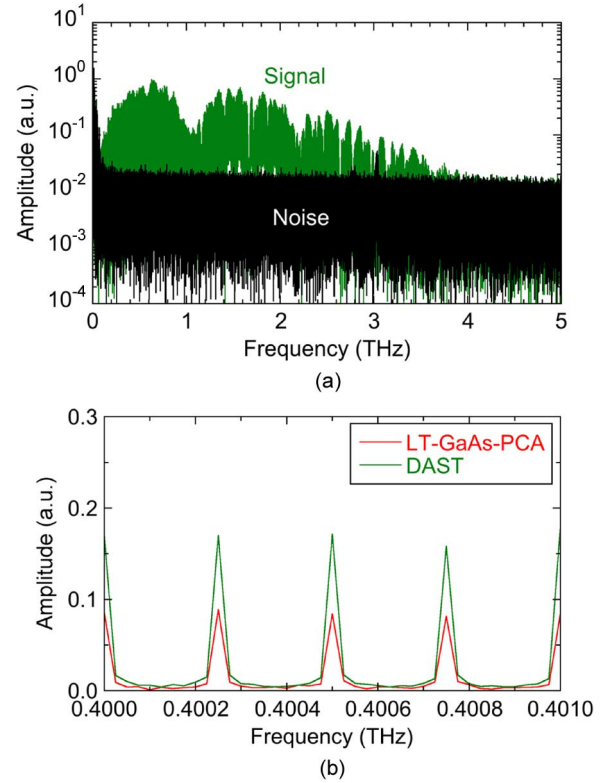

Fig. 5. (a) Amplitude spectrum of THz comb generated by DAST crystal. (b) Spectral comparison of THz comb mode around 0.4005 THz generated by LT-GaAs-PCA with one generated by DAST crystal.

Fig. 3(d). The THz comb modes have a frequency spacing of 250 MHz and a linewidth of 25 MHz. The frequency spacing was equal to the mode-locked frequency of the fiber laser, whereas the linewidth was consistent with the reciprocal of the temporal window in Fig. 3(a) (= 40 ns). Here the dynamic range of frequency scale DR_{freq} is defined as follows:

$$DR_{\text{freq}} = 20 \log \left(\frac{\text{spectral range}}{\text{sampling step of frequency}} \right) \leq DR_{\text{time}}. \tag{2}$$

In the case of Fig. 3(c) and (d), the DR_{freq} achieved is 98 dB from the sampling step of 25 MHz and the spectral range of 2 THz.

The time window was extended further to decrease the linewidth of the observed THz comb mode. Fig. 4(a) shows the acquired temporal waveform of the THz pulse train when the observed time window was extended to 400 ns (integration number = 5000, acquisition time = 10000 s). Since this time window was 100 times longer than one period of the THz pulse(= 4 ns), it contains 100 consecutive THz pulses. This time window corresponds to a mechanical time-delay scanning distance of 60 m if a conventional THz-TDS scheme was used, a distance that cannot be realistically achieved with a scanning stage. Even in the case of this incomparable time window, the accumulated timing jitter was 569 fs for the 100-th THz pulse in Fig. 4(a).

After taking the FT of the temporal waveform in Fig. 4(a), we expanded the spectral region around 0.5570 THz again, as shown in Fig. 4(b). Due to the increase of the time window(=

400 ns) a decreased linewidth of 2.5 MHz is observed for the THz comb modes, with an identical frequency spacing as in Fig. 3(d). In this case, DR_{freq} achieved is 118 dB from the sampling step of 2.5 MHz and the spectral range of 2 THz, which is incomparable performance in THz spectroscopy.

We also tried to extend the spectral bandwidth of THz comb by using a 4-N, N-dimetylamino-4′-N′-methyl stilbazolium tosylate (DAST) crystal (thickness = 240 μm) as a THz emitter instead of PCA1. In this experiment, we changed Δf to be 5 Hz. The green line of Fig. 5(a) shows the amplitude spectrum of the THz comb obtained by taking the FT of the temporal waveform of 10 consecutive THz pulses (integration number = 10 000, acquisition time = 2000 s). For comparison, an amplitude spectrum measured in the absence of the THz beam (noise spectrum) is shown as the black line in Fig. 5(a). The observed spectral bandwidth was extended up to 4 THz, which was twice as large as that in Fig. 3(c). This is because of the phase matching condition between THz pulse and 1.5 μm laser light in DAST crystal enhancing the THz spectral bandwidth [21]. Fig. 5(b) shows a spectral comparison of the THz comb mode around 0.4005 THz between DAST-based system and PCA1-based system. Absolute frequencies of THz comb modes in DAST crystal are strictly consistent with those in PCA1. This is because the absolute frequencies of all comb modes are secured by the rubidium frequency standard within a certain level of uncertainty, which depends on the stability of the temporal magnification factor (= $f_1/\Delta f$). Such the traceability to the frequency standard enables us to give the universal frequency scale on THz spectrum among different apparatuses.

B. Spectroscopy of Pharmaceutical Tablets

To evaluate the spectroscopic potential of THz comb, we recorded the absorption spectra of several pharmaceutical tablets because they display sharp spectral fingerprints in THz region resulting from their crystal structure. For the sake of this demonstration, we prepared two different sugar tablets (lactose and D-maltose powders mixed with polyethylene powder) and one reference tablet (polyethylene powder) with identical shapes (diameter = 10 mm and thickness = 1 mm). Sugar content by weight was 25% for D-maltose tablet and 50% for lactose tablet, respectively.

The red and blue lines in Fig. 6(a) and (b) shows amplitude spectra of THz comb after passing through the lactose tablet and the D-maltose one, respectively. For comparison, the amplitude spectrum of THz comb after passing through the reference tablet was also indicated as the black line in both graphs. Spectral dips clearly appeared in both spectra. Fig. 6(c) shows the absorption spectra of the two sugar tablets. Each absorption spectrum was calculated from envelop of power spectra of THz comb for the sugar tablet and the reference tablet. The two sugar tablets exhibited characteristic spectral fingerprints of THz absorption: 0.53 THz and 1.37 THz for the lactose and 1.10 THz for the D-maltose, in good agreement with the value reported in the literature [22]. In this way, it is possible to classify pharmaceutical tablets based on their spectral fingerprints appearing in THz comb even though they have a similar appearance.

C. Spectroscopy of Low-Pressure Molecular Gas

The demonstration in the previous section indicated a potential of THz comb spectroscopy for pharmaceutical applications. However, this demonstration does not necessarily make full use of advantages offered by THz comb spectroscopy because the spectral features of the pharmaceutical tablets are broader than the frequency interval between THz comb modes(= 250 MHz). From the viewpoint of high-precision THz spectroscopy, another interesting application is the analysis of atmospheric molecular gases, their rotational transitions give them particularly rich spectral fingerprints with much narrower linewidths in the THz region. To correctly measure these densely distributed absorption lines in THz spectroscopy requires high resolution, high accuracy, and broad spectral coverage.

To evaluate the potential of THz comb spectroscopy for gas analysis, the absorption spectrum of the rotational transition $1_{10} \leftarrow 1_{01}$ at 0.557 THz of water vapor was measured. To avoid pressure broadening of the absorption lines, water vapor was enclosed in a low-pressure gas cell (length = 500 mm, diameter = 40 mm). To decrease the strong absorption of water vapor, the water vapor was diluted in nitrogen gases. The partial pressures of water vapor and nitrogen were set to 0.6 kPa and 1.3 kPa respectively. We estimated the pressure broadening linewidth of this absorption line to be 250 MHz by the pressure broadening coefficient [23]. The red line in Fig. 7(a) shows amplitude spectrum of THz comb mode around 0.557 THz with the sample gas. Also, we obtained a reference spectrum with the vacuum cell as shown in the black line in Fig. 7(a). From comparison between them, decrease of spectral amplitude due to absorption of water vapor was confirmed across only two comb
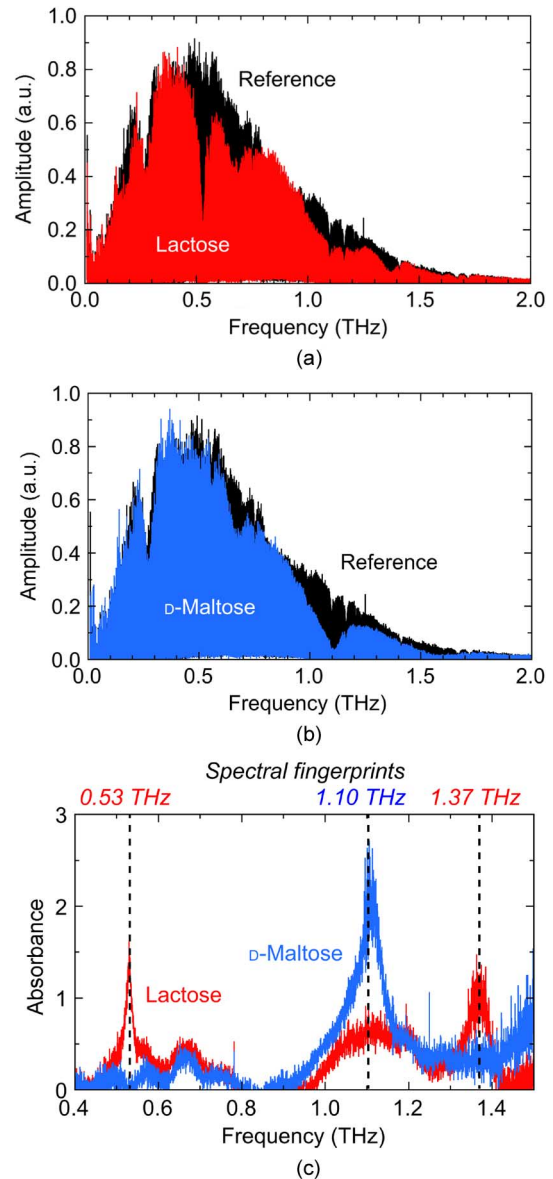

Fig. 6. Amplitude spectra of THz come after passing through (a) lactose tablet and (b) D-maltose one. (c) Comparison of absorbance spectra between lactose and D-maltose.

modes around 0.557 THz. The absorption spectrum was calculated by extracting peak of each comb mode of both spectra and normalizing water vapor spectrum by the reference spectrum as shown in Fig. 7(b). The spectral linewidth was determined to be 265 MHz when a Lorentzian function was fitted to the spectral shape, indicated by the red solid line in Fig. 7(b), which is consistent with the expected pressure broadening linewidth of 250 MHz. We estimated from the accumulated timing jitter of 105 fs and the time window of 40 ns that the contribution of the timing jitters to the spectral resolution was 66 Hz. The center frequency of this absorption spectrum determined by the curve fitting was 0.556858 THz, also in good agreement with the value reported in the literature(= 0.556936 THz) [24]. The deviation of 78 MHz from the literature values corresponds to the spectral accuracy of 10^{-4}. Here, it should be emphasized that this deviation is due to discrete distribution of comb modes at 250-MHz
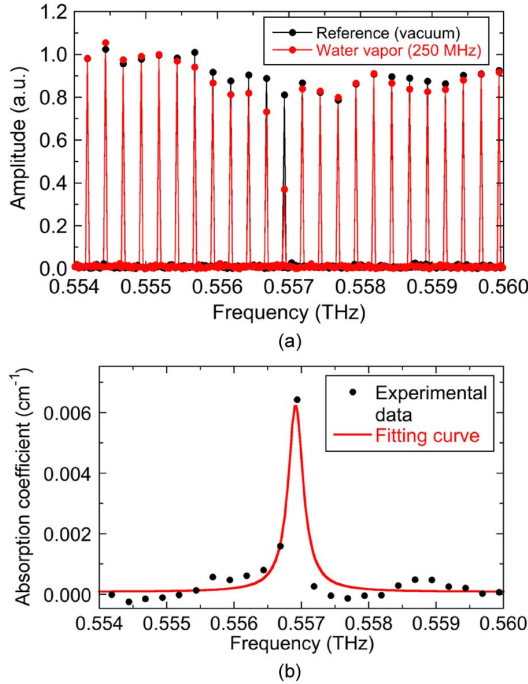
Fig. 7. (a) Amplitude spectrum and (b) absorption spectrum for the water rotational transition of $1_{10} \leftarrow 1_{01}$ at partial pressure of water vapor and nitrogen to be 0.6 and 1.3 kPa.

Fig. 8. (a) Absorption spectrum of acetonitrile gas at 40 Pa and (b) its magnified spectrum around 0.58 THz.

intervals, rather than uncertainty of absolute frequency of comb mode.

To demonstrate the capacity to simultaneously probe multiple absorption lines of low-pressure molecular gas, we performed gas-phase spectroscopy of acetonitrile (CH_3CN). As symmetric top molecule CH_3CN has a rotational constant B of 9.2 GHz [25], a manifold of rotational transitions regularly spaced by $2B(= 18.4 \text{ GHz})$ appears in THz region [26]. Fig. 8(a) shows the absorption spectrum of CH_3CN at 40 Pa. Many manifolds of the regularly spaced rotational transitions ($J = 16$ to 51) were clearly found within a frequency range from 0.3 to 1.0 THz. To observe the detailed structure of these absorption lines, we expanded the spectral region around 0.58 THz, as shown in Fig. 8(b). Two adjacent manifolds ($J = 30$ and 31) were clearly observed. The frequency separation between them was 18.4 GHz, is consistent with the $2B$ value of CH_3CN [26]. A small spike beside the manifold around 0.57 THz ($J = 30$) is caused by the electric noise in the current preamplifier. From these results, we can conclude that THz comb spectroscopy has a high potential for high-precision THz spectroscopy of low-pressure molecular gas.

V. DISCUSSION

One might feel that there is little difference between the THz comb spectroscopy and one-pulse-period ASOPS-THz-TDS [19]. Furthermore, another might think that repetitive THz pulse waveforms are only replicas of a single THz pulse waveform over one pulse period and thus cannot provide any more information than a one-pulse-period THz pulse waveform. Here we discuss the difference between the THz comb spectroscopy and one-pulse-period ASOPS-THz-TDS assuming that contribution of the timing jitter to the spectral resolution is negligible. On one hand, the spectral resolution
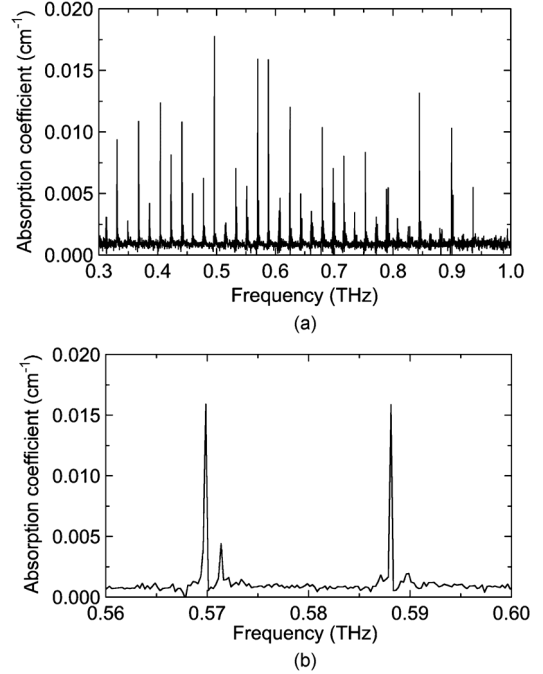
in one-pulse-period ASOPS-THz-TDS was equal to the laser mode-locked frequency f_1 [19]. In this case, each data plot on the spectrum was given as a mean value of the spectral amplitude over the f_1 intervals. On the other hand, THz comb spectroscopy provided the discrete spectra of THz comb mode with a linewidth of 25 MHz [see Fig. 3(d)]. The spectrum was obtained by sampling the spectral amplitude with the 10% width of f_1 at intervals of f_1. Therefore, the main difference between them is that the THz spectrum is composed of the averaging data for one-pulse-period ASOPS-THz-TDS and the sampling data for THz comb spectroscopy. Unfortunately, discrete distribution of THz comb mode limits the practical spectral resolution in THz spectroscopy to f_1 even though each data plot in the spectrum has the spectral resolution of 10% in f_1. However, the fact that individual comb modes were spectrally resolved will open the door for higher resolution THz spectroscopy over the broad spectral range based on narrow linewidth of the comb mode. Work is in progress to further decrease the spectral resolution in THz spectroscopy down to linewidth of comb mode.

VI. CONCLUSIONS

A THz comb has been employed as a precise frequency ruler for THz spectroscopy. The fine-structured spectrum of THz comb was obtained at good SNR by applying time-window-extended ASOPS-THz-TDS to temporal waveform measurement of THz pulse train with incomparable dynamic range of the time scale. To evaluate the spectroscopic potential of THz comb, we demonstrated the spectroscopy of pharmaceutical tablets and molecular gases. The individual spectral fingerprints of pharmaceutical tablets clearly appeared on the amplitude spectra of THz comb, to the best of our knowledge, this is the first experimental demonstration of THz comb spectroscopy. The results of low-pressure gas-phase spectroscopy indicate that the

established frequency scale is directly related to the THz comb structure, having frequency interval of 250 MHz and linewidth of 25 MHz in our case. The discrete distribution of THz comb modes limits the practical spectral resolution and accuracy in these demonstrations to be 250 MHz and 10^{-4}, respectively. Although the achieved resolution and accuracy may not be always sufficient for specific applications of high-precision THz spectroscopy, an assured traceability of the frequency scale to a microwave frequency standard is a significant advantage of this method over conventional THz spectroscopic methods without any traceability. These spectroscopic demonstrations make us conclude that the THz comb truly combines the merits of both THz-TDS and CW-THz spectrometers and has the strict traceability to a frequency standard. Furthermore, 25-MHz or 2.5-MHz linewidth of comb mode, which is much narrower than frequency interval between comb modes, implies the possibility to further enhance the spectral resolution and accuracy in THz comb spectroscopy. Therefore, THz comb opens the door for establishment of frequency metrology in THz spectroscopy.

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Yi-Da Hsieh received the Master's degree in biomedical imaging and radiological sciences from the National Yang-Ming University, Taiwan, in 2008, and is currently working toward the Ph.D. degree from the Graduate School of Engineering Science, Osaka University, Toyonaka, Japan.

His areas of research are THz instrumentation and gas-phase THz spectroscopy.

Mr. Hsieh is a member of the Japan Society of Applied Physics.

Yuki Iyonaga received the Bachelor's degree in mechanical science and bioengineering from the Osaka University, Toyonaka, Japan, in 2011, and is currently working toward the Master's degree from the Graduate School of Engineering Science, Osaka University, Toyonaka, Japan.

His areas of research are THz instrumentation and gas-phase THz spectroscopy.

Mr. Iyonaga is a member of the Japan Society of Applied Physics.

Yoshiyuki Sakaguchi is currently a Technical staff in Graduate School of Engineering Science, Osaka University, Toyonaka, Japan. His area of research is process technology for semiconductor device.

Mr. Sakaguchi is a member of the Japan Society of Applied Physics.

Shuko Yokoyama received the Ph.D. degree in mechanical engineering from the University of Tokushima, Tokushima, Japan, in 1996.

She is currently a CEO in Micro Optics Company, Ltd., Kyoto, Japan. Since 2006, she has been a Postdoctoral Researcher in the Department of Mechanical Science and Bioengineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Japan. Her areas of research are laser stabilization and optical metrology, particularly interferometry and measurement related to optical and THz frequency comb based on femtosecond laser.

Dr. Yokoyama is a member of the Japan Society of Applied Physics and the Optical Society of Japan. She received the Best Paper Award in Measurement Science and Technology from Institute of Physics in 1999.
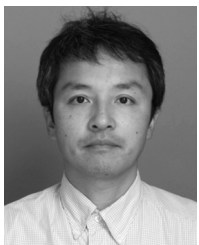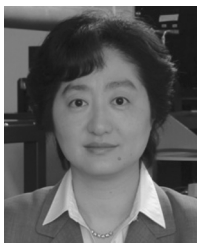
Hajime Inaba received the Ph.D. degree in applied physics from Hokkaido University, Sapporo, Japan, in 2004.

In 1993, he joined the National Research Laboratory of Metrology (NRLM, former AIST), Tsukuba, Japan, and he began work on continuous-wave erbium-doped fiber lasers. His areas of research are ultrafast optical science and technology and their application to optical metrology, particularly generation and control of frequency combs, and frequency metrology using frequency combs. He was a visiting scientist at the National Measurement Institute, Australia, between 2006 and 2007. He is currently a senior research scientist at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

Dr. Inaba is a member of the Japan Society of Applied Physics. He received a Prize for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology in 2008.

Kaoru Minoshima received the Ph.D. degree in physics from the University of Tokyo, Tokyo, Japan, in 1993.

She is at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, and also a Guest Professor of Tokyo University of Science, Japan. In 1993, she joined the National Research Laboratory of Metrology (NRLM, former AIST), was briefly with the University of Bordeaux I as an Invited Professor in 1996 and a Visiting Scientist at Massachusetts Institute of Technology, Cambridge, MA, USA, from 2000 to 2001. Her areas of research are ultrafast optical science and technology and their application to optical metrology, particularly time-resolved imaging, generation of frequency combs, and length metrology using frequency combs.

Dr. Minoshima is a member of the Japan Society of Applied Physics, the Physical Society of Japan, Laser Society of Japan, and the Optical Society (OSA). She served as one of the General Chairs and Program Chairs of CLEO conference in 2011 and 2009, respectively. She received a Prize for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology in 2008, and Women Researcher Award, The Japan Society of Applied Physics in 2010.

Francis Hindle received the Ph.D. degree in electrical engineering and electronics from the University of Manchester, U.K., in 2000.

He is appointed lecturer at the Laboratoire de PhysicoChimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France, in 2004. He has significant experience with THz instrumentation developing high-resolution spectrometers for gas phase applications.
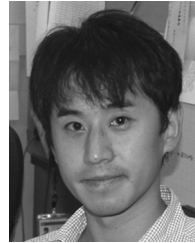
Yoshinori Takahashi received the B.S., M.S., and Ph.D. degrees in electrical engineering from Osaka University, Suita, Japan, in 1998, 2000, and 2007, respectively.

He is currently a Post-Doctoral Researcher in the Division of Electrical, Electronic and Information Engineering. His research interests include crystal growth of nonlinear optical crystals for ultraviolet light generation and THz wave generation, and medicinal compound.

Dr. Takahashi is a member of the Japan Society of Applied Physics and the Laser Society of Japan. He received the Lectures Encouragement Award from the Japan Society of Applied Physics in 2006, and the Progress Award from the Laser Society of Japan in 2012.

Masashi Yoshimura received the B.S., M.S., and Ph.D. degrees in electrical engineering from Osaka University, Suita, Japan, in 1994, 1996, and 1999, respectively.

He worked as an Assistant Professor from 1999 to 2007, and is currently an Associate Professor in the Division of Electrical, Electronic and Information Engineering. His research interests include development of new nonlinear optical crystals for ultraviolet light generation and THz wave generation.

Dr. Yoshimura is a member of the Optical Society (OSA), the Japan Society of Applied Physics, the Laser Society of Japan, and the Japanese Association for Crystal Growth. He received the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology in the Research Category in 2007, German Innovation Award Gottfried Wagener Prize 2012, and so on.

Yusuke Mori received the B.S., M.S., and Ph.D. degrees in electrical engineering from Osaka University, Suita, Japan, in 1989, 1991, and 1996, respectively.

He worked as an Assistant Professor from 1993 to 1999, a Lecturer from 1999 to 2000, an Associate Professor from 2000 to 2007, and is currently a Professor in the Division of Electrical, Electronic and Information Engineering. His research interests include crystal growth of nonlinear optical crystals for ultraviolet light generation and THz wave generation, protein, and gallium nitride. He is a Representative Director of SOSHO, Inc. since 2005.

Prof. Mori is a member of the Japan Society of Applied Physics, the Laser Society of Japan, and the Japanese Association for Crystal Growth. He received the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology in the Research Category in 2007 and 2008, German Innovation Award Gottfried Wagener Prize 2012, and so on.

Tsutomu Araki received the Ph.D. degree in applied physics from Osaka University, Suita, Japan, in 1977, and one in medical sciences from the University of Tokushima, Tokushima, Japan, in 1986.

From 1978 to 1979, he worked as a Post-Doctoral Fellow at the University of Wisconsin. He was with the Faculty of Medicine of the University of Tokushima from 1979 to 1987, and the Faculty of Engineering of the University of Tokushima from 1987 to 1996. He is currently a Professor in the Department of Mechanical Science and Bioengineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Japan. His research interests include development of a new biomedical and biophysical measurement system using a fast pulse laser.

Prof. Araki is a member of the Japan Society of Mechanical Engineers, the Japan Society of Medical Electronics and Biological Engineering, and the Japan Society of Applied Physics. He received the Sakamoto Award from the Japan Society of Medical Electronics and Biological Engineering, the Achievement Award from the Bioengineering Division in the Japan Society of Mechanical Engineers in 2006, the Achievement Award of Education and Research from the Osaka University in 2008, and the Funai Award from the Japan Society of Mechanical Engineers in 2009.

Takeshi Yasui received the Ph.D. degree in mechanical engineering from the University of Tokushima, Tokushima, Japan, in 1997.

From 1997 to 1999, he worked as a Post-Doctoral Research Fellow in the National Research Laboratory of Metrology, Japan. He was with the Graduate School of Engineering Science, Osaka University from 1999 to 2010, and was briefly with the University of Bordeaux I in 2007 and 2012, and with the University of Littoral Côte d'Opale in 2010 as an Invited Professor. He is currently a Professor in the Institute of Technology and Science, The University of Tokushima, Tokushima, Japan, and an Invited Professor in the Graduate School of Engineering Science, Osaka University, Toyonaka, Japan. His research interests include THz instrumentation and metrology, laser stabilization, nonlinear optical microscopy, and ultrafast time-resolved measurement.

Prof. Yasui is a member of the Optical Society (OSA), the Japan Society of Applied Physics, the Optical Society of Japan, the Laser Society of Japan, the Japan Society of Medical Electronics and Biological Engineering, the Japan Society of Mechanical Engineers, and the Institute of Electronics, Information and Communication Engineers. He received the Award for the Most Promising Young Scientist from the Optical Society of Japan in 1998, the Sakamoto Award from the Japan Society of Medical Electronics and Biological Engineering in 2006, the Optics Paper Award from the Japan Society of Applied Physics, and the Funai Award from the Japan Society of Mechanical Engineers in 2009.