INSTRUMENTS AND METHODS OF INVESTIGATION

High resolution terahertz spectroscopy for analytical applications

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Abstract. The latest achievements in the area of terahertz spectrometers based on transient effects are presented. The potential to use these spectrometers in various applications demanding the composition analysis of multicomponent gas mixtures simultaneously with a high sensitivity (at the ppb level) and resolving power is considered. The results obtained with the use of transient terahertz spectroscopy for medical diagnostics, security systems, etc. are shown.

Keywords: terahertz frequency range, high resolution spectroscopy, phase switching of radiation acting on gas, fast frequency sweep, multichannel spectroscopy method, multicomponent gas mixture, exhaled air, biological liquid vapors, medical diagnostics, vapors of high energy substances

1. Introduction

Microwave (or subterahertz, subTHz) and terahertz (THz) spectroscopy is a powerful tool for analytical research in chemistry and molecular physics. The microwave range of 10-100 Ghz was historically the first employed for analytical applications. The THz range spans the electromagnetic spectrum from 0.1 to 10 THz and lies between the microwave

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and infrared (IR) ranges. The main characteristics of the THz range comprise, first and foremost, intense absorption lines of rotational molecular motion, which makes this range topical for analytical chemistry. Furthermore, the low-frequency vibrational transitions of many heavy molecules also lie in the THz range. They are the vibrations of atom groups in large organic molecules and motions related to the vibrations of intermolecular hydrogen bonds. Due to their collective nature, these motions are highly sensitive to the intra- and intermolecular structures. They provide the unambiguity of determining the conformation state of a molecule and the effects related to its environment. Unlike the IR range, in which vibrational absorption bands are recorded, in the THz range it is possible to record absorption lines with a high resolution and unambiguously identify substances with a high degree of confidence. In addition, THz radiation is not an ionizing one and is therefore not hazardous to biological subjects, permitting its in vivo use, unlike the frequently used X-ray radiation. All these factors permit the use of THz spectrometers in many investigations: identification of biomolecules, including determination of their mutations and different conformation states; and the study of biological tissues, in particular, subsurface layers, which is directly related to the diagnostics of the depth of their damage (for instance, due to burns) and the presence of tumors, necrosis, and other pathological processes. Therefore, this range may be used for analytical studies of light and polyatomic molecules.

To analyze multicomponent gas mixtures, THz spectrometers should make use of synthesized signal sources and high-sensitivity detectors. The use of the optical approach resulted in the development of coherent radiation sources like optically pumped molecular lasers, free-electron lasers, and quantum cascade lasers (QCLs) [1-3]. The quasioptical approach provides a spectral resolution of about 0.1 cm⁻¹ (3 GHz) with frequency instability. For some applications which investigate the broad absorption bands, for instance, in semiconductor materials, this spectral resolution is sufficient. However, numerous problems in analytical chemistry, like

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the detection and measurement of the quantitative content of gases in multicomponent gas mixtures call for a high-resolution spectral analysis.

In developing the THz range, microwave methods occupy a special place. SubTHz sources like backward wave oscillators (BWOs) and frequency multiplication sources may cover ranges of up to 3 THz, but they may be rather bulky and high-power-consuming. Of special interest are synthesized THz sources owing to their low phase noise and improved spectral resolution, a high frequency stability, and frequency setting precision (to $10^{-9} - 10^{-11}$ of the carrier frequency).

Recent years have seen impressive progress in synthesized sources involving GaAs and GaN [4–10] Schottky diode production technologies with frequency multipliers up to 4 THz and above and with significant signal power levels [11]. Frequency multipliers based on GaN high electron mobility transistors (HEMTs) have not yet mastered the frequency range above 100 GHz. Radiation sources using monolithic microwave integrated circuits (MMICs) have also been demonstrated in the THz range at low frequencies [11– 13] but at a relatively low power level and with a very narrow spectral range.

Superlattices show promise for subTHz-to-THz signal frequency multiplication but require complex gold cavities for both the emitter and the detector, which significantly limits the frequency tuning and increases costs [14]. Integration of the device is extremely difficult, while the output power resulting from the multiplication is low. Photomixers provide only low-power outputs and are insufficiently tunable at high THz frequencies [14]. THz QCLs provide the output power and coherence required to detect gases [15], but wavelength tuning is extremely difficult and, moreover, cryogenic cooling is required [14]. Therefore, with modern technologies, the only solution for simultaneous generation in the subTHz–THz ranges is a combination of different types of sources in one spectrometer.

The method of difference frequency generation (DFG) due to the resonance optical nonlinearity with mid-IR QCLs shows the greatest promise for on-chip simultaneous radiation production from the THz to subTHz ranges [16, 17]. An analysis of the modern state of the THz radiation generation concept, which is outlined in Refs [18, 19] and involves the use of mid-IR distributed feedback (DFB) lasers, shows the feasibility of room-temperature operation in the 2.6–4.2 THz range with a THz output power of up to 0.1 mW. The highest output power was 1.4 mW, though without frequency tuning, with a single-chip scheme and in the pulsed mode [18, 19].

In comparison with the progress in subTHz and THz radiation sources, radiation detection technologies are noticeably lagging behind, since they are usually based on components which have their limits, like the temperature effect (for instance, Golay cells, bolometers, thermoelectric detectors) or a narrow range of electronic detectors (for instance, Schottky diodes in waveguide units). These limitations apply to either the sensitivity or the modulation range, or to both characteristics. The application of photoconducting switches based on low-temperature gallium arsenide (LT-GaAs) is the commonly accepted practice for continuous detection in the THz range with the use of near-IR lasers [20]. In recent years, various methods have been proposed for THz radiation detection [21, 22], which rely on such physical principles as intersubband transitions and related effects in quantum wells, superlattices, and quantum dots, tunneling with the participation of a photon in resonant-tunneling diodes, and photon detection using single-electron transistors and surface waves in high electron mobility transistors, etc.

Among all these developments and concepts, THz radiation detection with the use of field transitions shows good promise due to their well-confirmed sensitivity above 4 THz [22], the present record signal detection at 7 THz, the possibility of their monolithic integration in large arrays using complementary metal–oxide–semiconductor (CMOS) and monolithic microwave integrated circuit (MMIC) technologies, as well as the capability of their multifrequency operation.

High-resolution THz spectroscopy methods originate primarily from microwave physics. The first microwave Fourier spectrometers which offered high sensitivity and resolution were proposed by Ekkers and Flygare [23] in 1976, as well as by Balle and Flygare [24] in 1981. Since then, microwave instruments have been substantially improved and their application range extended to the THz range. The spectrometers operate using the effect of transient absorption, which appears when the radiation becomes resonant with a two-level system in a time shorter than the relaxation time, and transient emission, when the radiation goes out of resonance in a time shorter than the relaxation time. Therefore, by bringing the transition into resonance or taking it out of resonance, we obtain an alternation of the appearance and decay of macroscopic polarization. In this case, detected and analyzed is the freely decaying polarization signal, which contains information about the relaxation time and concentration of molecules.

Another effect used in transient experiments is the fast passage effect, when the frequency is swept across molecular resonance in a time shorter than the relaxation time [25]. One of the first papers reporting a fast passage experiment was Ref. [26], in which the authors also discussed absorption line reconstruction from detector signals. The key elements in the spectroscopic technique are the oscillators, which provide tunable radiation with a narrower line than the gas absorption linewidth. The majority of THz measurements are carried out on absorption lines whose linewidths range from several hundred kilohertz to several megahertz, and the probing radiation linewidth should therefore be of the order of several kilohertz.

2. Terahertz spectrometers based on transient effects

2.1 Spectrometer with phase manipulation of radiation acting on a gas

A high-resolution THz spectrometer may be realized by phase manipulation (PM) [27]. This spectrometer may operate in two modes: frequency scanning within a given range in search of the absorption lines of the components of a gas mixture or tracking changes in the absorption coefficient of a specific substance at the selected resonance frequency of the absorption line.

The phase manipulation mode consists of the following. Periodic switching of the phase (with a shift by π) or frequency of the radiation passing through a gas cell and resonantly interacting with the gas results in transient emission and absorption, i.e., in the periodic induction and decay of macroscopic polarization [28].



Figure 1. Structural diagram of a THz spectrometer with phase manipulation of the radiation acting on a gas with a BWO as a radiation source.

Transient signals in a spectrometer with phase manipulation are the same in each manipulation act. When the radiation frequency coincides with the molecular resonance frequency, the energy of radiating molecules is completely converted into the amplitude function of the radiation transmitted through the gas.

The resultant transient signal is recorded and accumulated in the receiving part of the spectrometer. To approximate the signal, use is made of the following formula [27]:

$$S(t) = \gamma l \frac{U_0}{\alpha(U_0)} \left(1 - 2 \exp\left(-\Gamma t\right) \right), \tag{1}$$

where U_0 is the measured DC voltage rectified by the detector, which is proportional to the radiation power P_0 at a low power ($P_0 < 100 \ \mu$ W). When the rectified DC voltage is relatively high, use is made of the correction coefficient $\alpha(U_0)$ ($\alpha = 1-2$). $\Gamma = 1/T_2$ is the halfwidth of the spectral line (T_2 is the polarization relaxation time of the gas molecules) and γ is the absorption coefficient. Γ and γ are spectroscopic parameters determined by way of approximation and *l* is the optical path length over which the radiation interacts with the substance under investigation (in the given configuration, *l* coincides with the measurement cell length). The magnitude and shape of these signals are employed to calculate the gas density.

The phase manipulation mode of the source radiation in a THz spectrometer should meet the following main requirements:

(1) In the course of manipulation, the phase shift should lie in the range $\pi \pm 0.1$.

(2) The duration of a PM must be at least an order of magnitude shorter than the relaxation time of the molecules under investigation, which typically lies between 0.2 and 2 μ s.

(3) The PM repetition frequency must be at least 3–10 times lower than the spectral line half-width T_2^{-1} , where T_2 is the transverse relaxation time.

(4) The operation of the PM system must not result in interference and failures in the frequency stabilization system of the radiation source.

(5) The phase shift should be automatically maintained equal to π for any changes in the radiation source operating



Figure 2. THz spectrometer with phase manipulation of the radiation acting on a gas with a BWO radiation source.

mode (scanning, frequency switching, changes in matching conditions, etc.).

To satisfy the requirements of high-resolution spectroscopy, the precision of setting the instantaneous source radiation frequency in the PM mode should be at least 10^{-8} of the resonance radiation frequency. This precision is achieved by using phase-locked loop (PLL) of the radiation source to a high-stability reference frequency synthesizer. This permits realizing the spectral resolution at a level of 10 kHz, required to unambiguously record and identify the absorption lines of many gases with a high resolution.

A structural diagram of a spectrometer with phase manipulation of the radiation acting on a gas equipped with a backward wave oscillator as the radiation source, as well as a spectrometer photograph, are displayed in Figs 1 and 2, respectively.

A PLL system is employed to automatically control the BWO frequency and the phase shift in the spectrometer. The spectrometer also comprises a system for recording in the time domain, averaging, and computer processing of the spectroscopic transient signal. The signal in the time domain is recorded in the spectrometer. Measurements may be carried out in two instrument modes: at a fixed frequency and in the scanning mode.

Among the virtues of a BWO as a radiation source is its relatively broad frequency generation range and high output power. A high output power is of importance when use is made of a frequency multiplier to perform measurements in higher-frequency ranges. Our spectrometer employed an OV-87 BWO (118–178 GHz) of a relatively small size and weight. The output signal power of the BWO amounts to several tens of milliwatts. Considering the loss in waveguide units, the output power of the signal exceeds 10 mW. This power level is high enough to employ a frequency multiplier. In measurements in the 118–178-GHz frequency range, an attenuator is mounted in place of the multiplier. Short circuit and high voltage breakdown protection circuits are built into the BWO power sources, characterized by a low level of interference and noise.

The spectrometer has a PLL system for controlling the BWO frequency. As a reference for the PLL system, use is made of a microwave frequency synthesizer F_{ref} , which forms a coarse frequency grid, and a digital frequency synthesizer (DFS) of intermediate frequency (IF), which forms a fine frequency grid F_{if} . The PLL–BWO circuit consists of a BWO, a directional coupler, a harmonic mixer, an intermediate frequency amplifier, and a frequency-phase detector (FPD). In the PLL, multiplication and mixing occur of the frequencies formed by the reference synthesizer and the IF synthesizer to obtain the following frequency at the BWO output:

$$F_{\rm BWO} = NF_{\rm ref} - F_{\rm if} \,, \tag{2}$$

where N is the harmonic number of the reference frequency synthesizer signal, $F_{\rm ref}$ is the reference synthesizer frequency, and $F_{\rm ref}$ is the IF frequency synthesizer.

The prescribed minimal frequency step at the BWO output is defined by the minimal frequency increment of the IF synthesizer. Both synthesizers (F_{ref}, F_{if}) have a common 10-MHz reference signal, whose characteristics affect the stability and accuracy of the output spectrometer frequency. To manipulate the phase of the BWO output frequency, throughout the frequency range the spectrometer employs phase manipulation of the IF synthesizer signal and the broadband PLL, which permits relaying the PM frequency from the IF synthesizer to the BWO output without distortions. The phase manipulation is realized with the help of a phase modulator, which is inserted between the IF synthesizer and the FPD input. The input system of the phase modulator generates the timing triggering signal. The FPD operates in the frequency band of the IFA (10-300 MHz). The output FPD signal passes through the active PIF and the buffer amplifier. Then, the signal is delivered directly to the BWO anode, which is electrically insulated from the rest of the units of the instrument. In this case, it changes the BWO frequency, thereby keeping the PLL system in the state of synchronism. The PLL control band in the synchronism mode amounts to at least 2.5 MHz for the entire BWO frequency operating range.

The receiving part of the spectrometer comprises an amplitude detector, a DC amplifier, a video amplifier, and a receiving system. The signals at the output of the measuring cell after the detector are amplified by the video amplifier and fed to the receiving system of the spectrometer. In the receiving system, their analog-to-digital conversion occurs via a 'fast' analog-to-digital converter (ADC), digital averaging, and data transfer to a computer. The analog signal, which carries information about the rectified voltage at the detector, is delivered to the input of a slow ADC via a DC amplifier.

2.2 Spectrometer with semiconductor devices based on high-resolution terahertz spectroscopy methods

We designed and made a compact spectrometer utilizing semiconductor devices for high-resolution THz spectroscopy intended for analyzing multicomponent gas mixtures, including the vapors of explosives, as well as the composition of air exhaled by a person. A distinctive feature of this spectrometer is its compactness and the possibility of using it as a sensor to detect a selected set of substances, which is topical for medical and biological tasks.

A structural diagram and photograph of a spectrometer with a heterodyne receiver are given in Figs 3 and 4, respectively.

The spectrometer is made using only semiconductor elements. The radiation source and the local oscillator are based on Gunn oscillators with the use of quantum semiconductor superlattice (QSSL) frequency multipliers and have similar setups. The radiation source and the local oscillator differ only in the frequency of the reference oscillator for the PLL system. The frequency of the reference oscillator in the signal source is 260 MHz and the frequency in the local oscillator is 200 MHz. As a result, the frequencies of the signals at the output of the Gunn oscillators are $f_1 = Nf_0 + 260$ MHz and $f_2 = Nf_0 + 200$ MHz, respectively. Due to this difference, the source frequency is shifted by 60 MHz relative to the heterodyne, and this difference is independent of the frequency of the reference synthesizer.

The QSSL frequency multiplier of the radiation source produces several harmonics. Use is usually made of harmonics with numbers *M* from 3 to 7.

The heterodyne receiver is made employing a QSSL mixer. For a local oscillator, use is made of a Gunn oscillator whose frequency is stabilized to the reference frequency synthesizer and the PLL-2 (see Fig. 3). The PLL-2 operates as follows. The Gunn oscillator signal is mixed in the harmonic mixer with the Nth harmonic of the reference synthesizer of frequency f_0 . The intermediate frequency signal is fed to the PLL-2 system and compared with the reference oscillator signal using a phase detector (PD). The signal from the PD output is delivered via correction filters to the input of the control of the Gunn oscillator frequency, thereby closing the PLL. Formed at the mixer output are IF signals equal to the difference between the frequency of the received signal and the heterodyne signal frequency, which are equal to the difference between the harmonics of the source and heterodyne:

$$f_{\rm if} = M f_1 - M f_2 = M \times 60 \text{ MHz}$$
, where $M = 3 - 7$.

Accordingly, the IF will assume values from 180 to 420 MHz, inclusively.

After amplification, these signals are delivered to the signal receiving system and next to a computer for accumulation and processing. To record the signal arising from a gas absorption line, the modulation of the reference source oscillator signal is used. This modulation is transferred to the output of the Gunn oscillator via the PLL-1 system. In the



Figure 3. Structural diagram of a THz spectrometer based on semiconductor elements.



Figure 4. THz spectrometer based on semiconductor elements.

course of reception, the signals are demodulated in the recording system. Controlling the synthesizer frequency by the PC permits selecting the frequency ranges with intense absorption lines of the selected gases.

2.3 Fast frequency sweep spectrometer

We designed and implemented a THz spectrometer based on the effect of fast frequency sweep (Fig. 5). The spectrometer is intended for recording the absorption spectrum of a multicomponent gas mixture throughout the spectrometer operating range (118–178 GHz). The recording time is of the order of several seconds, making it possible to detect the initial, intermediate, and final products of fast chemical reactions.

For a source of radiation acting on a gas, use is made of an OV-79 backward wave oscillator (Research and Production Corporation Istok) for the two-millimeter wavelength range (118–178 GHz). The BWO is powered by a high-voltage (0.3–1.6 kV) source, the voltage defining the BWO frequency.

To control the BWO frequency, a control signal is applied either to the reference input of the high-voltage power supply (the low-frequency control channel) or directly to the BWO anode, which is connected to the instrument housing via a low (50 Ohm) resistance (the broadband control channel).

To meet the requirements of high-resolution spectroscopy, the accuracy of setting the instantaneous BWO frequency in the course of a fast sweep should be better than 10^{-6} of the resonance radiation frequency. In order to attain this accuracy, use should be made of BWO automatic frequency control (AFC) using a highly stable reference oscillator. As such, use is made of a reference frequency synthesizer (8–12 GHz), whose signal is mixed with the BWO signal in a harmonic mixer. The intermediate frequency signal from the mixer output is amplified and fed into an IF prescaler, where its frequency is divided by 4 or 16 or passes without change. The division factor depends on the necessary sweep range, which may vary from 10 to 1500 MHz. The divided IF signal transformed to transistor-transistor logic (TTL) levels suited for digital processing is delivered to the input of the unit, intended for the digital processing of the IF signal. The digital processing unit contains the key elements of the automatic BWO-frequency tuning unit, a digital frequency detector (provides a coarse frequency tuning in the course of PLL 'capture'), a digital phase detector (provides the phase BWO synchronization, on average during the sweep time, to the reference frequency synthesizer), and a digital deviation detector (provides a fine tuning of the sweep range). This unit also contains a circuit for the digital recording of the IF signal made around a shift register and random-access memory (RAM).

The data of the shift register are used to precisely determine the frequency-time dependence after enabling the AFC system and setting the sweep mode. The digital processing unit is based on modern programmable logic integrated circuits (PLICs) from Altera (USA).

To form a fast sweep signal (the voltage controlling the BWO frequency sweep), use is made of an AD768 fast 16-bit digital-to-analog converter (DAC) from Analog Devices, which produces a signal of nearly triangular shape at its output. To compensate for the BWO characteristic nonlinearity, in the general case the shape of the fast sweep signal differs from the triangular one. The data prepared beforehand are periodically read from RAM and delivered to the DAC. The reference DAC voltage and hence the amplitude of the fast sweep signal are defined by the voltage applied from the output of the deviation detector. The thus formed



Figure 5. Structural diagram of a spectrometer with a fast frequency sweep.

feedback sets the magnitude of the fast sweep signal such that the sweep range corresponds to the prescribed one. To minimize the quantization errors introduced by the DAC, its output signal passes through an electronically controlled attenuator (the BWO control unit), which is used when the prescribed sweep range is less than one half of the maximal one. The fast sweep signal is applied to the input of the broadband BWO control channel.

The output signals from the frequency and phase detectors are delivered to the BWO control unit, where they are filtered and amplified, and are applied in parallel to the inputs of both BWO control channels, thereby closing the phase-locked loop of the BWO.

The receiving spectrometer part comprises a detector module and a digital receiving unit.

The detector module contains a detector head with a Schottky diode, a low-noise preamplifier with a circuit for applying bias to the detector, and a low pass filter (LPF). Measuring the rectified DC voltage at the detector (at the LPF input) makes it possible to determine the spectral line intensities without any preliminary calibrations.

Broadband spectroscopic signals (0.1–12 MHz) from the preamplifier output are delivered to the input of a fast AD-9050 10-bit ADC from Analog Devices. Data from the ADC are fed to fast digital storage, which performs summation and real-time averaging of the spectroscopic signals. The sampling frequency of the ADC and digital storage is 25 MHz. The storage sums every 64 signals and transfers the data to the computer, where averaging may be continued. Coherent signal accumulation permits improving the signal-to-noise ratio and, hence, the sensitivity of spectroscopic measurements.

A built-in computer module executes control and monitoring of the main spectrometer units, as well as the processing of spectroscopic signals. The data exchange between the computer and spectrometer units is performed via an industrial standard architecture (ISA) bus using the corresponding controllers. The use of subTHz and THz spectroscopy based on the effect of fast sweep of radiation frequency across molecular resonance lines yields a high sensitivity and vast spectroscopic information in the analytical investigation of multicomponent gas mixtures, spectral investigation of molecular beams, and investigation of fast processes.

2.4 Two-channel spectrometer

The concept of a two-channel spectrometer with two independent radiation sources (based on 118–178-GHz BWOs), a common receiving unit, and a signal processing unit was proposed for the simultaneous study of the density dynamics of two components of a multicomponent gas mixture (Fig. 6). Both sources operate in the phase manipulation mode. The radiation from the first and second synthesizers is alternately applied to a measuring cell with separation of phase switching at a time sufficient for signal decay due to transient processes in the gas after irradiation by the previous pulse [29].

Two spectrometer versions were developed. The first one uses two identical BWO radiation sources in a range of 118–178 GHz. Inserted in one of the channels is a frequency tripler, which operates in the range of 330–390 GHz. Both sources are independent BWO-based frequency synthesizers with PLL to the signals of a reference synthesizer. The reference synthesizer for a range of 8–15 GHz provides spectral purity and frequency tuning.

The synthesizers are controlled via an I2C control bus. The intermediate frequency (IF) between the reference synthesizer harmonic frequencies and the BWO frequency is fed to the PLL system. Directly applied to the other input of the PLL unit is the signal from a digital frequency synthesizer (DFS) in a frequency range of 110–130 MHz, which provides fine frequency tuning. The DFS is controlled via a parallel bus for improving the new frequency loading. The BWO frequency is tuned by varying the voltage across the retarding system of the BWO. The BWO power supply units are controlled via the DAC of the controller. The signals from



Figure 6. Structural diagram of a two-channel THz spectrometer.

both sources are summed in a directional coupler (10 dB) and applied to a horn antenna via a focusing lens. The antenna directivity exceeds 35 dB. The signal from the second 118–178-GHz radiation source is attenuated in a directional coupler by 10 dB. For an output BWO power above 20 mW, the output power of the signal from the directional coupler amounts to 2–3 mW. This is sufficient for exciting gas molecules.

The summary signal from the sources with radiation phase manipulation passes through a 1-m-long quartz cell to a broadband detector. The detector is based on a low-barrier diode with a Schottky barrier and exhibits a high sensitivity of $500-2500 \text{ V W}^{-1}$, as well as a broad frequency range of 100-1200 GHz. A hemispherical silicon crystal lens provides detector matching to the recorded radiation.

Measurements are performed under permanent evacuation of the studied gas mixture. The output detector signal contains information about the initial radiation power in the bias and information about the radiation absorption by gas molecules in the form of a broadband video signal. The total signal is split by filters and amplified by a preamplifier. After the preamplifier, the output signals are fed to the receiver inputs, which constitute the input of a fast ADC for the video signal and the input of a slow ADC for the bias. The digital signals are averaged in a digital storage device and then applied to a computer for processing and storage.

The receiving unit is a computer unit made in the form of a plug-in shielded module fitting the Eurocard standard. Inside the module are two electronic boards:

• a communication controller with a PCM-3362 computer module from ADVANTECH (PRC).

• a circuit board with a 250-Gb hard disk on it. On the front panel of the module are connectors for communication with peripheral devices: VGA, PS/2 ETH (Ethernet), USB (two ports).

The PCM-3362 computer used in the spectrum analyzer was made in the PC/104 design. The PC/104 printed circuit

board (PCB) measures slightly more than 90×90 mm. A PCB of this size is conveniently built into the Eurocard (the height of a Eurocard PCB is 100 mm).

The PCM-3362 single-board computer is intended for controlling the units of the spectrum analyzer and processing the measurement data, which arrive by the internal spectrum analyzer bus from the receiving unit to the spectrum analyzer via a communication controller.

The spectrometer allows temporal separation of signals from different gas absorption lines. The period *T* of recording signals for two gas absorption lines is 4 μ s. The temporal separation mechanism makes possible the simultaneous detection of up to eight gases (*T* = 16 μ s), with provision of eight radiation sources required in this case. The video signal from the PM-signal-excited absorption line decays exponentially. The time *T* is selected so that the signal from the first absorption line decays completely by the time the signal from the second absorption line appears.

The two-channel spectrometer can operate in a broadband mode, scanning two frequency regions simultaneously, as well as in the mode of recording the temporal dynamics of the signal at a frequency corresponding to an analytical gas absorption line.

The spectrometer may operate in a combined mode, i.e., the program offers two graphics windows: one shows the temporal dependence of the absorption coefficient of the first gas, while the second window may depict the absorption spectrum in the scanning mode.

The detector voltages and absorption coefficients at a certain frequency are indicated in the program window.

2.5 Terahertz spectrometer with a quantum cascade laser

Figures 7 and 8 depict the structural diagrams of different versions of high-resolution THz spectrometers based on quantum cascade lasers. Implementing spectrometers with the use of sources like QCLs permits spectroscopic measurements to be performed in the region above 1 THz, where it is



Figure 7. Structural diagram of a THz spectrometer comprising an HEB and a QCL with a PLL system.



Figure 8. Structural diagram of a THz spectrometer based on an HEB and a QCL with frequency stabilization to a gas absorption line. AFC: automatic frequency control.

possible to record not only rotational but also low-lying vibrational absorption lines. Developing a transient highresolution THz spectrometer requires single-mode THz QCLs with a working temperature as high as possible (at present, THz QCLs operate at helium temperatures) and an output power of several tens of milliwatts, as well as with an improved directivity and structure. An important goal in the design of a QCL-based precision radiation source is the development of a phase-locked-loop frequency control system (see Fig. 7). A successful version of a QCL PLL system (a 3rd-order distributed feedback single-mode QCL with a frequency of 3.4 THz) was reported in Ref. [30]. The main components of the PLL are a phase detector unit, a frequency detector unit, and a control unit. The QCL is accommodated in a helium cryostat with a 1.2-mm-thick high-density polyethylene window. The THz QCL radiation is directed to a harmonic mixer, which is located outside of the cryostat, via two high-density polyethylene lenses, which are used in the standard telescopic configuration to focus the THz radiation on the horn of the harmonic mixer. The experiment on the PLL QCL with an output frequency of 3.4 THz was performed using room-temperature electronics. The PLL system was designed and implemented with the use of a QSSL harmonic mixer cooled to a temperature of 10 K (a 3rd-order distributed feedback QCL at a frequency of 4.7 THz with low power consumption (0.5 mW) and an output power of about 0.25 mW) [31]. The QCL and the QSSL harmonic mixer were accommodated next to each other in the helium cryostat.

Also required to control QCL emission is a fast frequency modulation system connected to the PLL system. The QCL THz radiation source used to excite molecules may also be employed as a local oscillator, which requires the development of a low-noise broadband mixer and its integration with the QCL.

In another version of a THz radiation source employed in the prototype of a THz spectrometer, it is proposed to employ a QCL with frequency stabilization to the absorption line of a gas (water, NO) (see Fig. 8).

The QCL radiation with frequency modulation passes through a reference gas cell and arrives at a superlattice-based detector. At the resonance curve, the frequency-modulated (FM) signal transforms into an amplitude-modulated (AM) one, whose phase depends on the relative position of the radiation frequency and the absorption line frequency. The requirements for the modulation frequency and the frequency deviation are such that they should be comparable to the width of the reference gas absorption line at a pressure corresponding to the working pressure in the cell intended for the realization of the transient spectroscopic method. The modulation frequency is provided by a modulated signal oscillator and the deviation by a device for controlling the amplitude and phase of the modulated signal. The phase control should span the $0^{\circ} - 180^{\circ}$ range. At the PD output, a signal appears whose polarity and amplitude depend on the relative position of the radiation frequency and the absorption line frequency. Next, via an LPF and a frequency adder, this signal is relayed to the power supply of the QCL and changes its frequency in the requisite direction.

Detection is performed with a heterodyne receiver based on a hot-electron bolometer (HEB). For a heterodyne, use is made of a 118–178-GHz BWO-based frequency synthesizer and a frequency multiplier based on semiconductor superlattices, with the multiplier placed in a cryostat. Next follows computerized data processing. The key problem in setting up this spectrometer consists in the optimization of the working parameters of the units and devices that make up the spectrometer.

2.6 Terahertz spectrometer based on a phase diffusion field

Stochastic fields may play a 'constructive' role in their interaction with quantum systems. A spectrometer based on the effect of a THz phase-diffusion field (PDF), which induces macroscopic polarization in the gas under investigation, was designed and implemented (Fig. 9) [32]. Making this spectrometer does not call for the use of a reference oscillator or for the development of radiation source modulation and stabilization systems, since the source is a noise oscillator based on superconducting structures. Scanning the frequency range is limited by the bandwidth of the noise source.

The radiation source which was developed and employed in this experiment was an 'oscillator' realized with the use of a sequence of internal Josephson contacts based on $Bi_2Sr_2CaCu_2O_8$ (BiSCCO) structures. The internal Josephson contact was formed in a BiSCCO structure cell with CuO₂ layers, which were superconducting electrodes, and with BiO and SrO layers, which made up the barrier layer [33]. The 1-µm-thick crystal contained about 670 internal Josephson contacts. In 2007, it was reported that such sets (stacks) can emit coherent radiation at frequencies above 0.85 THz with a directly detectable power of about 10 nW [34]. The stack of internal Josephson contacts used in THz experiments



Figure 9. Structural diagram of a PDF spectrometer: 1 — oscillator based on a BiSCCO mesa structure, 2 — superconducting integral detector mounted on a silicon lens 3, 4 — input and output Maylar windows of cryostats.

was made of a low-doped BiSCCO crystal grown by the floating zone technique [34]. Some significant stages of the procedure are outlined below. A 200-nm-thick gold layer was deposited on the surface of the chip of a single BiSCCO crystal, which was glued to a silicon substrate with epoxy resin. Then, a sample was etched with the use of photolithography and argon ion milling on a 1.1-µm-thick rectangularshaped mesa structure $350 \times 70 \ \mu m$ in size. At the next stage, the sample was fixed on a second substrate of MgO with epoxy resin and then transferred to the MgO substrate by spalling from its gold-coated lower surface. The freshly chipped surface was directly coated with a 100-nm-thick gold layer. Eventually, the photoresist area measuring $300 \times 210 \,\mu\text{m}$ was patterned using photolithographic etching. As a result, a 1.1-µm-thick mesa structure with transverse dimensions of $300 \times 70 \ \mu m$ was obtained, which had contacts with the upper and lower gold layers [35].

To perform high-resolution spectral measurements, a superconducting integral receiver (SIR) was used [36, 37]. The SIR [36] accommodates on one chip a low-noise superconductor-insulator-superconductor (SIS) mixer with a quasi-optical antenna, a superconducting local oscillator, and a second harmonic SIS mixer (HM) for the phase locking of the superconducting local oscillator. All components of the SIR microcircuit were made using a high-quality Nb-based triple layer on one chip on a silicon substrate. The receiver chip is located on the plane surface of a silicon lens, which makes up an integrated lens antenna. The phase-locked local oscillator is continuously tunable throughout the 300-750-GHz range. The output power of the superconducting local oscillator is sufficient for pumping the related SIS mixer in a broad frequency range and is electronically adjustable. The measured linewidth of the free running superconducting local oscillator ranges between 0.3 and 5 MHz. Due to optimization of the receiver, the measured noise temperature in the two side channels is lower than 100 K, i.e., about $4 hf/k_{\rm B}$; the intermediate frequency range is 4–8 GHz and spectral resolution is under 1 MHz [37]. These parameters furnish the possibility of developing an integrated receiver for the 450-650-GHz range for different applications [37-39]. When measuring the ammonia line (572 GHz), the SIR frequency was phase-locked to 566 GHz, while the intermediate frequency was about 6.5 GHz.

The high sensitivity and spectral resolution of the developed spectrometers make possible their use for many applications: medicine and biology, hi-tech, and security systems. In this case, it is possible to perform combined spectroscopic investigations. For instance, in the analysis of a multicomponent gas mixture of unknown composition, it is possible to employ a spectrometer with a fast frequency sweep, which records all absorption lines of substances throughout its operating range in a time of the order of several seconds. The next stage is the use of a phase manipulation spectrometer in two working modes: performed initially is frequency scanning in the selected frequency range to verify the data obtained with the fast-sweep spectrometer and identification of absorption lines, and then it is possible to study the dynamics of the absorption coefficient of a specific substance at the frequency of a resonance absorption line. Even more opportunities open up with the use of a two-channel spectrometer, which permits combining the modes of spectrum recording, detecting two substances simultaneously, and tracking their dynamics in a mixture. Based on the resultant data, a THz spectrometer based on semiconductor elements may be employed as a sensor of specific gases. The phase-diffusion field spectrometer and the quantum-cascade laser spectrometer furnish advancement to the higher-frequency region.

3. Application of transient-effect spectrometers

Among the wealth of analytical tasks which may be solved by high-resolution THz spectroscopy, mention should be made of fundamental problems like measurements of the resonance frequency and intensity of absorption lines of a substance; determination of rotational constants, dipole moment components, and self-broadening and broadening coefficients of the absorption lines of substances; identification and investigation of conformers and isotopes; and structural investigations of molecular complexes. A special place is occupied by the chemistry of the interstellar medium. It delves into, first of all, the inner regions of gas-dust molecular clouds, where conditions exist for the formation and existence of complex molecules.

The interstellar medium is investigated with telescopes operating in the microwave, subTHz, and THz ranges: ALMA, Herschel, SOFIA, APEX, etc. At present, carried out in laboratory conditions are measurements and preliminary estimates of the spectra of simple astrophysical molecules, for instance H_2S [40] and HD [41], as well as of complex ones, like metal acetylenides [42] and organic isocyanides [43]. Of prime interest are gases that widely occur in the regions of star formation. Another category of interstellar gases of prime interest are molecules important for prebiotic chemistry, which may permit approaching the discovery of the origin of terrestrial life [44, 45].

High-resolution THz spectroscopy has enjoyed wide use in solving biological and medical problems. Investigations of biological and biologically active molecules in the gas phase provide information about their initial structure unaffected by the environment and thereby furnishes the possibility of discovering the intramolecular factors that control molecular properties as well as structural and functional relationships. Recent years have seen a rapid development of noninvasive medical diagnostics reliant on the analysis of exhaled air. Based on the presence of one marker or another in the air sample exhaled by a patient, it permits diagnosing illnesses and controlling the course of treatment. Diagnostic techniques have been developed for some socially significant diseases (diabetes, oncological and



Figure 10. Record of acetone absorption line in the air sample exhaled by a patient with type 2 diabetes.

gastroenterological diseases) [46, 47]. Investigations have shown the high content of acetone (Fig. 10) and ethyl and methyl alcohol in the breath of patients with diabetes in comparison with healthy people. Furthermore, the dynamics of the acetone density prior to and after the admission of medicines have been revealed. Observed in this case was an insignificant variation in the density of alcohols in exhaled air [48].

Samples of air exhaled by conventionally healthy nonsmoking volunteers and cancer patients (Hodgkin's lymphoma, central endobronchial lung cancer) were analyzed in

 Table 1. NO concentration in the air exhaled by conventionally healthy volunteers and cancer patients.

No.	NO concentration prior to radiation therapy session, vol. %	NO concentration after radiation therapy session, vol. %						
Conventionally healthy volunteers								
1	0.00717 ± 0.00036							
2	0.00538 ± 0.00027							
3	0.00747 ± 0.00037							
4	0.00329 ± 0.00017							
5 0.00327 ± 0.00016								
Hodgkin's lymphoma, stage II								
1	0.012 ± 0.0006	0.022 ± 0.0011						
2	0.0149 ± 0.00075	0.0254 ± 0.0013						
Central endobronchial lung cancer, stage III								
1	0.018 ± 0.0009	0.075 ± 0.00375						
2	0.015 ± 0.00075	0.034 ± 0.0017						
3	0.0179 ± 0.0009	0.0747 ± 0.00374						
4	0.0149 ± 0.00075	0.0335 ± 0.00168						
5	$0.0254 \pm 0.0013 \qquad \qquad 0.0508 \pm 0.00254$							
Central endobronchial lung cancer, stage IV								
1	0.12 ± 0.006	0.224 ± 0.0112						

clinical conditions prior to and after radiation therapy. The measurement data are collected in Table 1. A low NO concentration was observed in the air exhaled by healthy people and the growth of the concentration of this substance for cancer patients. The NO concentration was measured not for the purpose of diagnosing lung cancer but for studying the dynamics of its content in the exhaled air prior to and after a radiation therapy session for patients who underwent irradiation of the mediastinum area and lung tissue in connection with different oncological diseases (lung cancer, Hodgkin's lymphoma). The resultant data revealed a significant (by a factor of 2–5) increase in NO content immediately after irradiation, which confirmed the hypothesis about the role played by this compound in the development of radiation-induced damage to biological tissues [46].

Experiments to discover acetone, methanol, ethanol, and hydrogen sulphide in air samples exhaled by diabetes patients, which were performed using the developed spectrometers, showed the promise of research in the quest for metabolite markers in exhaled air and the vapor of biological liquids that unambiguously characterize the presence of diabetes [49].

Jointly with the V A Almazov National Medical Research Center (St. Petersburg, Russia), an experimental investigation was made of samples of exhaled air and urine vapor using a transient THz spectrometer with phase manipulation of the radiation acting on a gas, with a BWO (OV-86, 118–178 GHz) radiation source. Figure 11 shows the experimental setup based on a transient THz spectrometer employed to measure the acetone concentration in the samples of exhaled air and urine. The vapor of a substance under investigation was admitted into the measurement volume by attaching a container with the substance to the spectrometer via a needle leak valve and continuous gas evacuation from the gas cell using a vacuum pump. The working gas pressure was 10^{-2} mbar.

This spectral investigation resulted in the discovery of marker lines typical of type-II diabetes (acetone, ethanol, methanol).

To investigate the gas composition of the liquid vapor, measurements were made of the rotational spectra of substances in the range of 118–178 GHz. The instrument operated in two modes:

(1) Frequency scanning mode with the option of selecting the frequency range, the frequency increment, and signal accumulation. Recorded in this case were the rotational spectra of the substances that occur in urine vapor samples.



Figure 11. Transient THz spectrometer experimental setup used for measuring the acetone concentration in samples of exhaled air and urine.



Figure 12. Simultaneous measurements of acetone concentration in the samples of exhaled air and urine at frequencies of 151,646.597 MHz (a) and 150,534.629 MHz (b).

(2) Useful signal accumulation mode at the resonance frequency of a marker line in the rotational spectrum (for instance, acetone). Accumulation and averaging of the signal in time permitted obtaining the marker line intensity with a high accuracy.

The data of simultaneous measurements of acetone concentration in the samples of exhaled air and urine for diabetes patients are given in Fig. 12.

Measurements of acetone content in the samples of exhaled air and urine have demonstrated the promise of using THz spectroscopy for medical diagnostics, of diabetes in particular. Performing clinical investigations of the composition of exhaled air and urine for type-2 diabetes patients will aid in the search for marker molecule combinations characterizing the patient's condition.

The high spectral resolution of THz spectrometers and precise information about absorption line frequencies provide trustworthy detection of gases in atmospheric air. The application of spectroscopic techniques in atmospheric chemistry covers the detection and monitoring of the atmospheric air composition, pollutants, and components of explosives and chemical weapons. In the framework of the European TErahertz and submillimeter LImb Sounder (TELIS) program, a mobile spectrometer was developed and launched on a balloon to measure the profiles of some trace gases (H₂O¹⁸, HDO, BrO, ClO, O₃, HCl) in the stratosphere [50]. The spectral characteristics of atmospheric pollutants were measured [51]. Special emphasis was placed on the development of high-sensitivity instruments for detecting and analyzing toxic substances and components of explosives and chemical weapons [52]. Investigations were made of the spectra of common poisonous substances and chemical weapons components (soman, sarin, and lewisite), as well as of the products of their natural decomposition and main impurities (Fig. 13) [53, 54].

A high-resolution THz spectrometer was employed to investigate the absorption spectra of the vapors and products of natural and thermal decomposition of explosives like



Figure 13. Portions of the subTHz spectrum of lewisite decomposition products: (a) in the 147.125–147.145-GHz range, (b) in the 160–164.5-GHz range, where 1 - 2-chlorovinylarsine oxide, $2 - \beta$ -chlorovinyl arsenic acid, $3 - \beta$ -propionitrile.



Figure 14. Record of the absorption line of formaldehyde, which is one of the thermal decomposition products of octogen.

ammonium nitrate, octogen, hexogen, trinitrotoluene, and pentaerythritol tetranitrate. Potential marker substances were revealed for their remote detection in the atmosphere (Figs 14–16), and the thermolysis kinetics of these substances were studied [55–58].

The lines of acetone (140,264.2 MHz) and diethyl ether (140,273.1 MHz) were identified. The 140,251.6-MHz line is yet to be identified.



Figure 15. Record of a portion of the absorption spectrum of the thermal decomposition products of pentaerythritol tetranitrate.



Figure 16. Record of a portion of the absorption spectrum of the thermal decomposition products of hexogen.

4. Conclusions

We have presented a review of gas spectrometers developed for the subTHz and THz frequency ranges and have demonstrated their virtues, which include simultaneously realized high sensitivity and resolving power.

The advantages of using high-resolution THz spectroscopy techniques for analytical applications were demonstrated. In analytical chemistry, for instance, this involves obtaining quantitative information about the molecular structure and strong absorption lines, and detecting conformers and isotopes. High-resolution THz spectroscopy plays an important role in studies of molecular dynamics and clusters. This approach is used in the identification of molecules in astronomical observations. The appearance of biological applications favors the understanding of structural and functional relations important for biochemistry. Furthermore, this approach is nondestructive for a gas sample under investigation.

Broad avenues open up in solving problems like detecting trace gas concentrations in multicomponent mixtures, for

instance, detecting impurities in high-purity substances, remote detection of the vapors of explosives, etc. However, also required is high sensitivity (at ppb or even ppt levels), apart from a high resolution. The general strategy of spectroscopic technique development along these lines involves the use of high-sensitivity detectors, preconcentration, and multipass gas cells.

The sensitivity and reliability of spectral analysis may be improved by combining THz and IR spectroscopic methods. Employing achievements in modern semiconductor electronics permits making a combined spectrometer with IR and THz radiation sources reliant on quantum cascade lasers and semiconductor nanostructures, which may be used to detect in the two frequency regions the absorption lines of the substance under investigation, thereby providing a highly reliable analysis.

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