

Terahertz Spectroscopy System of Gas Mixtures Based on a Solid State Superconducting Source and a Terahertz Receiver

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Abstract—The application of a Josephson generator of the terahertz range based on a long superconductor–insulator–superconductor tunnel junction matched with a transmitting antenna and emitting a signal into open space is demonstrated for gas spectroscopy. The generator is used as an active source, the signal of which is absorbed by a sample of a gas mixture in a cell with a length of 60 cm and then recorded by a spectrometer based on a superconductor–insulator–superconductor receiver with a spectral resolution better than 100 kHz. In the experiment, the absorption lines of ammonia and water in the terahertz range were recorded, and the dependence of the spectral characteristics of the absorption lines on the pressure of the gas mixture in a wide range (from 0.005 to 10 mbar) was demonstrated.

Keywords: terahertz sources and receivers, Josephson effect, absorption spectroscopy, gas analysis

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INTRODUCTION

Today, spectroscopy in the terahertz (THz) range is actively used in a wide range of tasks, from the study of condensed matter physics to the construction of biomedical images. There are books and reviews devoted entirely to the principles and applications of this method [1–3]. For instance, THz spectroscopy is used in physics and material science to study the dynamics of charge transfer in various semiconductor structures, such as heterojunctions, quantum dots, nanocrystals [1, 2], in superconductors and strongly correlated electron systems [1]. The processes of electrical conductivity and photoproductivity in various materials are studied using THz spectroscopy [3]. Applications in analytical chemistry and medicine include spectroscopy of biological tissues and samples, pharmaceutical studies [3]. THz radiation is used in security systems for detecting explosives, substances [4], and for constructing images in the THz range [2, 3]. Since THz radiation is nondestructive, it is actively used in biological systems to study vibrational modes that propagate through large parts of biomolecular structures (proteins, RNA, DNA) with lengths up to tens of angstroms [5]. The studied phenomena are important for the functioning of biomaterials that undergo transformations in secondary and tertiary structures.

Such a wide range of applications of THz spectroscopy encourages the creation of new methods and devices. Some time ago, our group proposed and implemented the concept of an flux-flow oscillator (FFO) based on a long Josephson junction (LJJ) of the superconductor–insulator–superconductor (SIS) type, coordinated on a single chip with a transmitting antenna and a harmonic mixer (HM) for phase stabilization of the output signal [6–10]. The operating frequency f of the source is controlled within a sufficiently wide range by a constant bias voltage V at the junction, which is related to the frequency by means of the Josephson constant 483.6 GHz/mV:

$$f = (2e/h)V,$$

where h is the Planck constant and e is the electron charge. The radiation power of such a generator ranges from hundreds of nanowatts to units of microwatts [11] in a spectral band with a width of hundreds of kilohertz to ten megahertz in the autonomous generation mode. To narrow the spectral line of the emission, a phase locking loop (PLL) is traditionally used, which stabilizes up to 97% of the power in a narrow peak with a width of about 40 kHz. The generation frequency ranges from 250 to 700 GHz with the possibility of continuous tuning by controlling the local magnetic field and the displacement current. The radiation characteristics of the source were studied by three principally different methods: using an external

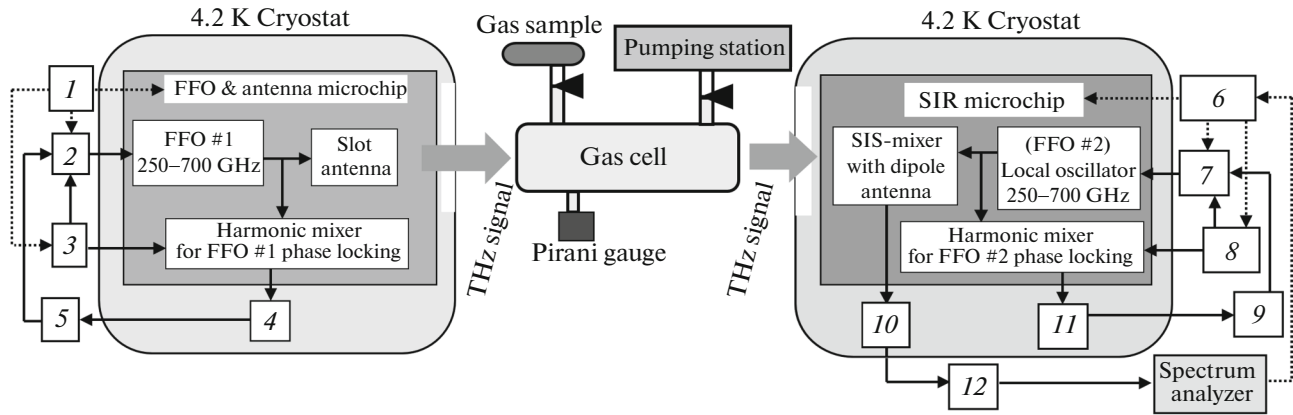


Fig. 1. Diagram of an experimental setup for recording gas absorption lines in the THz range based on an FFO source and a SIR-based spectrometer. The main elements of the scheme are decrypted on the drawing; auxiliary elements: (1, 6) PCs; (2, 7) PLL systems; (3, 8) microwave reference generators: 20 GHz for the harmonic mixer and 400 MHz for the PLL; (4, 10, 11) cryogenic (4.2 K) IF signal amplifiers for the SIS mixer based on transistors with high electron mobility; (5, 12) IF signal amplifiers for the harmonic mixer of the 0–800 MHz range operating at room temperature; (9) signal amplifier for the IF of the 4–8 GHz range operating at room temperature.

broadband cooled bolometer based on silicon [9–11], using a THz spectrometer with a resolution of about 40 kHz based on the SIS detector with a heterodyne [7, 8], as well as using a feedback system with a generator via a harmonic mixer and a PLL system [7, 8]. Each method was used to study different characteristics.

The developed generator seems to be a practical solution as an external source of the THz range for use in spectroscopy, microscopy, and image construction. In this paper, we demonstrate the applicability of such a source for spectroscopy in an experiment on the registration of gas absorption lines. The closest application of the shown technique is the study of the composition of exhaled air, on the basis of which it is possible to identify marker substances and diagnose certain diseases [12–14].

GAS REGISTRATION SYSTEM BASED ON THZ SPECTROSCOPY AND RESEARCH METHOD

The system for recording gas absorption lines uses an active solid-state THz radiation source based on LJJ, described in detail, for example, in [7, 10], and a superconducting integrated receiver (SIR) with high sensitivity based on a SIS junction [15, 16]. The scheme of this multi-element system is shown in Fig. 1. A similar scheme was used, for example, in [17] with an active source based on a reverse wave lamp, as well as in the works [18, 19] with an active source based on high-temperature single-crystal superconductors. An “initial” output signal of the FFO #1 passes through a measuring cell with the gas under study and is detected by a THz spectrometer after some absorption caused by rotational junctions of the gas mole-

cules. The cell length is 60 cm, the cell windows are made of Teflon, transparent in the THz range. The width of the absorption line largely depends on the gas pressure, which is set by the intake and pumping speeds and is measured by a Pirani vacuum meter. It should be noted that the system has an additional signal absorption by air in the room, mainly by water vapor, which, however, did not affect the experiment due to the too wide line at atmospheric pressure, which makes a homogeneous contribution to the absorption in the frequency band of the analysis and does not affect the shape of the recorded spectrum. The intermediate frequency (IF) range of the receiver is 4–8 GHz with the center, respectively, at 6 GHz. The spectrum of the absorbed signal is eventually recorded by the spectrum analyzer in the IF range. The method of recording absorption spectra is as follows. The frequency of the receiver heterodyne (FFO #2 in Fig. 1) is set to 6 GHz above or below the absorption frequency of the gas under study (for example, 578.5 GHz for the ammonia absorption frequency of 572.5 GHz), and the frequency of the active source (FFO #1 in Fig. 1) gradually changes in a narrow range (for example, ± 0.5 –1 GHz) in the vicinity of the absorption frequency in both directions. The spectrum analyzer operates in the mode of recording the maximum value of the peak of the radiation line, so that the peak power is recorded at each scanning frequency, as shown in Fig. 2a. If gas is present in the measuring cell and its pressure is sufficient for detection, a clearly defined minimum is observed on the recorded curve, as shown in Fig. 2b. When the cell is pumped out to a high vacuum, the spectrum analyzer records a relatively flat frequency dependence (see the dashed line in Fig. 2b), which is used later as a reference curve for processing the results. Since the IF out-

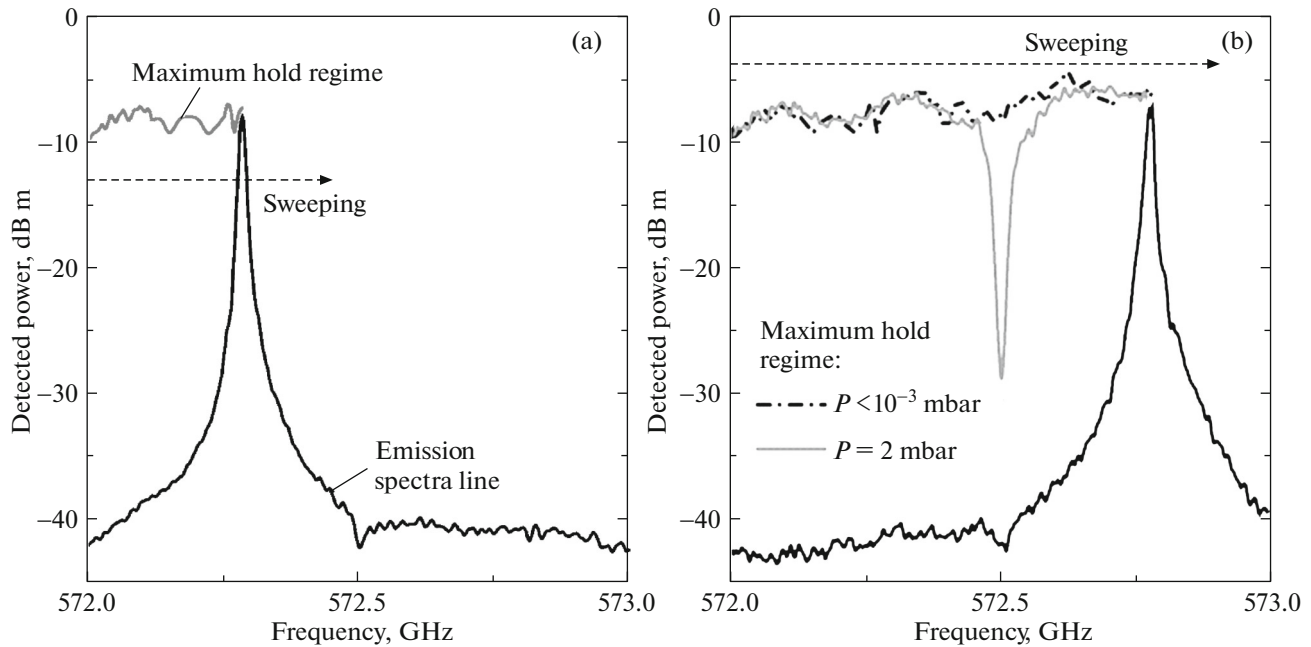


Fig. 2. Process of recording the gas absorption line in the recording mode of the maximum peak value of the spectrum analyzer by the method of frequency scanning from left to right: (a) radiation frequency of the generator is less than the absorption frequency; (b) radiation frequency of the generator exceeds the absorption frequency.

put signal is not perfectly uniform in frequency due to the natural frequency characteristics of the microwave amplifiers and the presence of standing waves in the output path of the receiver, the recorded dependence of the maximum peak value in the absence of gas (the reference curve) is also not perfectly flat.

This procedure is repeated several times at different gas pressure, after which the reference curve is subtracted from the recorded curve at each pressure to bring the signal to the level of 0 dB in the absence of absorption.

RESULTS

Results of detection of absorption lines of ammonia (NH_3) and water (H_2O) at frequencies of 572.5 and 556.9 GHz, respectively, are shown in Fig. 3. An readily available medical aqueous ten percent solution was used as an ammonia sample, therefore, the partial pressure of the ammonia itself is lower than the total pressure of the mixture recorded by the vacuum meter. Distilled water is used as a water sample, so the recorded pressure is the true water vapor pressure with adjustments for the measurement error and the calibration coefficients of the Pirani sensor for different gases. The gas inlet into the cell is carried out by natural evaporation of the liquid in a test tube connected to the inlet pipe of the cell through a needle flow with smooth adjustment. Before the gas intake, the cell was preliminary evacuated to a pressure below 10^{-5} mbar (the measurement limit of the Pirani vacuum meter)

for 10–15 min. Figure 3 demonstrates the broadening of the spectra and an increase in the absorption power with an increase in gas pressure. The characteristic half-width of the ammonia absorption line at a pressure of 0.5 mbar was about 8 MHz. The characteristic pressure in the experiment varied from $\sim 10^{-3}$ mbar to about 20 mbar: at a higher pressure, the absorption line was still observed, but its spectral width was too large due to collisional broadening. The limiting pressures for detecting gases in the conducted experiment were about 0.05 mbar for ammonia and 0.005 mbar for water. The duration of one measurement, equal to the time of the frequency passage up and back down, was about 2 min for each pressure value.

It is interesting to note the fact that the line width of the active source based on the LJJ is practically unimportant in this experiment, it is only important that the frequency scanning step is less than the line width for more accurate recording of curves in the recording mode of the maximum peak value, and also that the time spent by the generator at each point in frequency is sufficient, taking into account the recording speed of the spectrum analyzer. Thus, the characteristic line width in the experiment with ammonia was about 15 MHz (the line spectrum is shown in Fig. 2) and about 12 MHz in the experiment with water. The width of the source line begins to play a role only when the radiation leads to saturation of the receiver, which can affect the accuracy of the results. Source stabilization based on the PLL system and the harmonic mixer is available, but is not used in this fre-

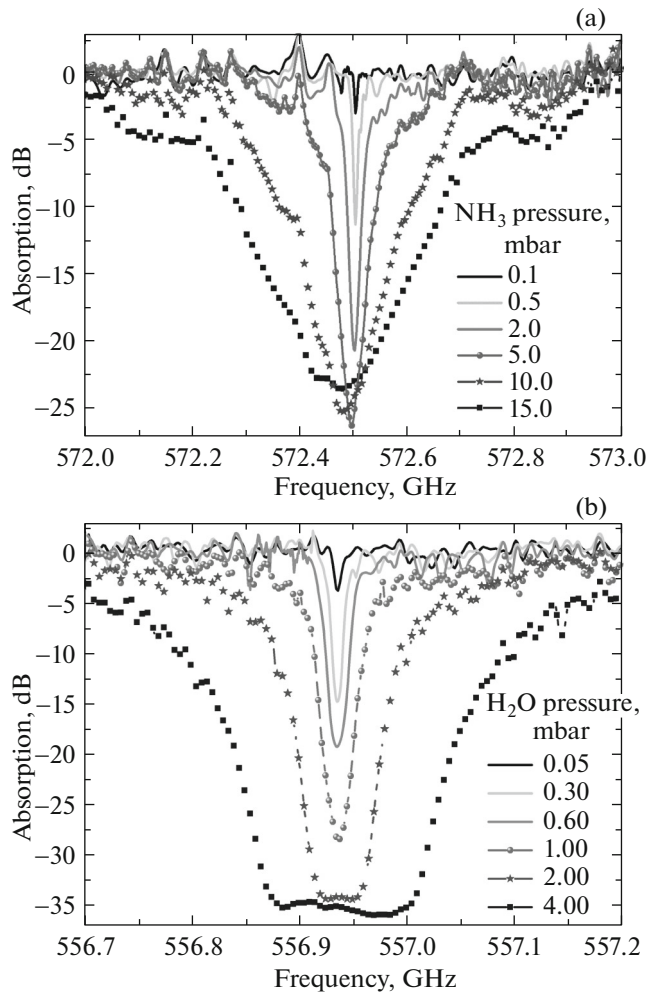


Fig. 3. Absorption spectra recorded by the system based on an LJJ source and a THz spectrometer at different pressure levels: (a) 10% aqueous solution of ammonia and (b) distilled water.

quency scanning technique. The obtained characteristics, absorption frequency, power, width of spectral lines, agree well to the reference literature and tabulated values.

The spectral resolution of the proposed method is determined by the resolution of the SIR with a phase-stabilized heterodyne based on its own LJJ; this resolution is better than 100 kHz [15]. The conducted experiment demonstrates that the spectral resolution and sensitivity of this gas detection system are close to the characteristics of other systems or exceed them, including, for example, systems based on quantum cascade lasers from [20] and Fourier spectrometers based on chirped pulses [21]. Finally, it is worth noting that the gas pressure sensitivity demonstrated in this work can be improved by one or two orders of magnitude when using a different reading system and with additional modulation of the active source based on the LJJ. In particular, in this work, the spectrum ana-

lyzer was used as an terminal device for recording absorption curves, and the presence or absence of gas was visually assessed on the analyzer screen. From the point of view of sensitivity, this method is far from the maximum achievable parameters. To increase the sensitivity, one can use a microwave power meter or a spectrometer based on a fast Fourier transform, as well as accumulate the signal for a long time and increase the number of passes of the absorption line when scanning the frequency. Nevertheless, the conducted experiment demonstrates the potential applicability of the THz gas spectroscopy system for a whole range of tasks, such as medical diagnostics using the registration of marker substances in exhaled air, control of technological processes, gas leaks, and environmental monitoring.

CONCLUSIONS

In this paper, we have developed a system for detecting gases in a gas mixture based on the absorption spectroscopy in the THz frequency range. As an active source, we used a previously developed widely tunable solid-state generator based on a LJJ. A superconducting integrated receiver based on a SIS junction was used as a detector, and the final analysis device was a spectrum analyzer operating in the output frequency band of the receiver 4–8 GHz. Based on this system, the registration of an ammonia absorption line at a frequency of 572.5 GHz with a maximum recorded pressure of about 0.05 mbar, and water at a frequency of 556.9 GHz with a maximum recorded pressure of about 0.005 mbar was demonstrated. The application areas of this gas analysis method are proposed, such as the diagnosis of certain diseases by the study of exhaled air, technological and environmental monitoring.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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