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Molecular gas spectroscopy using radioacoustic detection and high-power coherent subterahertz radiation sources

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ABSTRACT

We study the "power" approach to improve the sensitivity of the radioacoustic detection method by increasing the radiation power. A gyrotron is the source of high-power continuous monochromatic radiation in the spectrometer. As a result of analysis of experimental profiles of known lines of the rotational SO_2 spectrum, it was demonstrated for the first time that an increase of radiation power by about three orders of magnitude leads to a proportional increase of the RAD spectrometer sensitivity. This permitted us, in particular, to observe the weak transitions predicted earlier in the SO_2 molecule.

1. Introduction

Sensitivity is one of the key parameters of any spectrometer, which determines the range of its possible applications for resolving both fundamental and applied problems. High resolution of the gas spectrometers permits one to observe the lines which characterize unambiguously, as fingerprints, the particular molecules. This opens up huge opportunities, on the one hand, for a molecular-level understanding of the world and, on the other hand, for a quantitative and qualitative analysis of the gas mixtures. The higher the sensitivity, the higher the accuracy of measurement of the spectral line parameters and the greater the number of lines that can be observed in the experiment (the smaller the number of molecules in a gas mixture needed for their lines to appear in the spectrum) and the higher the accuracy with which the properties of the molecules can be explored. High sensitivity of the spectrometer can significantly extend the range of studied objects. Apart from the conventional electric- and/or magnetic-dipole transitions of the molecules, there is a huge number of the so-called forbidden transitions, including those which become allowed due to a centrifugal disturbance in symmetric top and spherical molecules, as well as quadrupole transitions, which are even weaker. The latter are currently little studied and only the observation of several lines of a few molecules confirms their existence. For example, a record sensitivity of about $5 \cdot 10^{-13}$ cm^{-1} (with a signal accumulation time of 4.5 days) was achieved in the IR range by the method of CRD (Cavity Ring Down) spectroscopy [1], which made it possible to perform for the first time highly accurate line shape study [2] of a series of the electric-quadrupole transitions of the hydrogen molecule and demonstrate necessity of further refinement of the most popular nowadays HTP model [3].

One can recall quite a large number of currently known wideband spectrometers used for a study of the spectra of various molecules in the mm/submm wave range. They can be divided into two types according to the principle of molecular spectra registering: from variations in the characteristics of either radiation or the gas being studied [4].

For most of the mm/submm spectrometers, in which either the radiation transmitted through a cell with gas or the radiation re-radiated by the gas is detected, a sensitivity close to the limit determined by fundamental physical principles is achieved (see, e.g. [5], chapter 15, p. 414). The only method that permits one to advance in solving the problem of high sensitivity achievement is known as optoacoustic (photoacoustic or radioacoustic) detection of absorption [6]. For example, a twentyfold increase in sensitivity of the optoacoustic spectroscopic method with the radiated power increased from 0.7 to 15 mW was demonstrated in the IR region [7]. The development of the technology and methods of photoacoustic spectroscopy has found wide practical application, in particular, for the problems of micro-impurity analysis (see, e.g., a

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review paper [8]). On the basis of this method, a spectrometer with radioacoustic detection of absorption signal (RAD spectrometer) was developed more than forty years ago, and has successfully been operated up to now, in the mm/submm range [4,9,10].

The sensitivity of any spectrometer is determined by several factors. The most crucial ones are radiation power, detection system noise (which may depend on the mean radiation power), and spectral purity of the radiation (directly related to the radiation noise). In spectrometers of the first type (e.g., classical video-spectrometer), the sensitivity increases with increasing radiation power until the detection system noise becomes surpassed by the radiation noise. The further increase in power is not practical because a useful signal starts increasing simultaneously with noise, while the sensitivity remains the same. For example, one does not need more than an about 1-mW radiation power in the mm-submm wavelength range if the source is referenced by the phase locking system to a contemporary ultralow-noise microwave synthesizer, and a liquid helium-cooled bolometer serves as a radiation detector. The situation is radically different in spectrometers of the second type (e.g., in a RAD spectrometer). In this case, the detection noise is defined by thermal fluctuations of a microphone membrane in the gas (both due to the inherent Brownian motion of the membrane and the Brownian motion of the gas). The limiting sensitivity of the spectrometer is obtained when thermal fluctuations of the membrane are defined preferably by the Brownian motion of the gas. These fluctuations do not depend on the radiation power passing through the gas cell. Meanwhile, the useful signal amplitude is directly proportional to the radiation power absorbed by the gas and, therefore, linearly increases with the power. Thus, the RAD sensitivity of RAD, or, in other words, the signal-to-noise ratio of the spectral lines observed by the RAD, is also linearly increasing.

In this paper, we report on the step towards the super-sensitive detection in the mm-submm wavelength range by increasing the radiation power by orders of magnitude. This is a mutual feature of any spectrometer of the second type. This is absolutely impossible in spectrometers of the first type, namely, because of the detector noise increase (followed by the detector burning) with increasing power. We demonstrate the feasibility of significant (several orders of magnitude) improvement of RAD spectrometer sensitivity by using high-power coherent radiation sources. The sensitivity achieved in the spectrometer permitted us, in particular, to observe the weak transitions predicted earlier in the rotational spectrum of the SO_2 molecule.

2. Spectrometer with radioacoustic detection: principles

A detailed description of the modern version of the RAD spectrometer and methods for studying the spectral properties of gases can be found in [11]. We will give only a short description of the device. A simplified diagram of the RAD spectrometer is shown in Fig. 1.

By tradition, backward-wave oscillators (BWOs) are used as radiation sources in the RAD spectrometers, a series of which covers a very wide range of 35–1500 GHz ([12,13], http://www.istokmw.ru/). The BWO power can vary from a fraction to tens of mW (reaching more than 100 mW in the best tubes) within the operating frequency range. High stability, low level of the phase noise, and exact knowledge of the frequency are provided due to the use of a phase-locked loop (PLL) system of the BWO radiation referenced by a microwave frequency synthesizer signal, which is synchronized with a frequency and time standard signal [14,15]. The detector of absorbed radiation power is a cell with gas and a microphone connected to it. If the radiation frequency coincides with the molecular transition frequency, then the gas absorbs the radiation, is heated, and expanded. Pressure variations are registered by a microphone. Radiation frequency or amplitude modulation and the synchronous detection of absorption signal are used for increasing the spectrometer sensitivity. The output signal of the spectrometer is directly proportional to the power of the radiation absorbed by the gas. The signal can be expressed as a product of the incident power of the radiation, gas absorption coefficient and optical path length, if the Beer-Lambert law is taken into account and the case of a small optical depth is considered.

Thus, there are two methods to improve the sensitivity of the RAD spectrometer, namely, to increase the effective optical path length and/or radiation power. Let us examine both methods.

A standard approach for improving the sensitivity of any spectrometer is to increase the optical path length in the gas. This is commonly done by using gas cells of different length (from a few centimeters to tens of meters) and configurations (e.g., White and Heriott multipass cells, resonator-type cells, etc.). A sensitivity increase in the RAD spectrometer with increasing effective path length was examined in [16–18]. As a result, a record sensitivity of $3 \cdot 10^{-11}$ cm^{-1} of the RAD spectrometer for a synchronous detection time constant of 1 s and a radiation power of about 50 mW was demonstrated in [17] by observation of pure rotational lines of the N_2O molecule in excited vibrational states (030) and (040) in a resonator-type gas cell. The main drawback of using high-Q resonators, unlike the multipass cells employed in the IR range, is the need to adjust the resonance frequency to the scanned radiation frequency. This method is difficult to use when unknown low-intensity lines are sought, but it can be fully utilized in a particular gas analysis since the frequency of the marker line is well known in advance. In addition, the resonance cell significantly complicates the interference pattern in the wave channel of the spectrometer and hence complicates the spectrometer baseline. This makes it virtually impossible to use resonant cells for a high-precision analysis of the molecular line profiles.

Another way for improving the sensitivity of the radioacoustic method is to increase the radiation power. However, unlike the IR range, the choice of mm/submm radiation sources is not as wide even at present. The following paragraph presents a short review of available powerful generators.

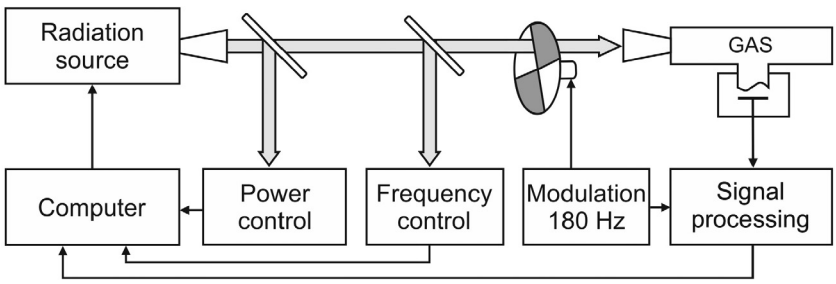

Fig. 1. Simplified diagram of the RAD spectrometer.