

THE METRIC OF SUBMILLIMETER RANGE OF WAVELENGTHS USING A REFERENCE SPECTRUM

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Methods are considered for using a reference spectrum to measure the power of coherent radiation and the frequencies and intensities of the spectral lines of gases in the submillimeter range of wavelengths, which are based on the use of a radiospectroscope with an acoustic detector. The proposed methods considerably expand the possibilities of a submillimeter-range metric. The merits of these methods include: 1) simplicity, which allows easy automation of the measurement process; 2) the possibility of performing measurements of all of the indicated quantities simultaneously at a large number of points over the range for a short operating time of the submillimeter equipment.

1. A radiospectroscope with broadband backward-wave tubes (BWT) and an acoustic detector which records the pressure variation of the gas during absorption of radiation by it (RAD) [1] allows automatic two-channel recording of the absorption spectra of molecules to be performed in a continuous range from 150 to 870 GHz ($\lambda = 2-0.35$ mm). The volume thermal character of the reception ensures frequency independence and averaging of interference effects. The recordings of the spectra contain thousands of lines, the signal-to-noise ratio reaching 10^5-10^6 . The magnitude of the signal from the spectral line is equal to

$$A = KP(1 - e^{-\gamma l}), \quad (1)$$

where K is the frequency-independent RAD constant; P is the power of the microwave-radiation generator; γ is the absorption coefficient of the gas line per unit length; l is the length of the cell containing the gas ($l \sim 10$ cm).

2. The rotational absorption spectrum of the sulfur dioxide molecule SO_2 is used as the natural scale of frequencies and intensities of the spectral line (i.e., as the reference spectrum) in the submillimeter range of wavelengths. The most abundant isotopic varieties $\text{S}^{32}\text{O}_2^{16}$ and $\text{S}^{34}\text{O}_2^{16}$ have a rotational spectrum that is not complicated by a hyperfine structure and can be described well within the framework of the asymmetrical-nonrigid-top model. This allows frequencies in the submillimeter range to be calculated with a relative accuracy of better than 10^{-6} and calculation of the intensities of the spectral lines with a relative accuracy of the order of 10^{-2} using numerous measurements at lower frequencies. The quantity of impurities in the sulfur dioxide obtained by the method expounded in [2] is of the order of 1% molar, it being true that the great bulk of this is water (H_2O) and sulfur trioxide (SO_3). The rotational spectrum of water is very spread out due to the smallness of the moments of inertia and has been thoroughly studied [3]. The dipole moments of sulfur trioxide is equal to zero, and consequently the rotational spectrum is not present in the electrodipole approximation. The authors obtained a continuous recording of the SO_2 spectrum in the 265-370 GHz range in which about 500 lines with the absorption coefficient $\gamma \approx 10^{-4}-10^{-2}$ cm^{-1} belonging to the isotopic combination $\text{S}^{32}\text{O}_2^{16}$ which is in the ground and three lower vibrational states [(010), (020), (100)] and to the isotopic combination $\text{S}^{34}\text{O}_2^{16}$ which is in the ground vibrational state have been identified. The identified lines are arranged fairly uniformly with an average density of 1 line per 250 MHz. A sector of the recording of the spectrum is displayed in Fig. 1.

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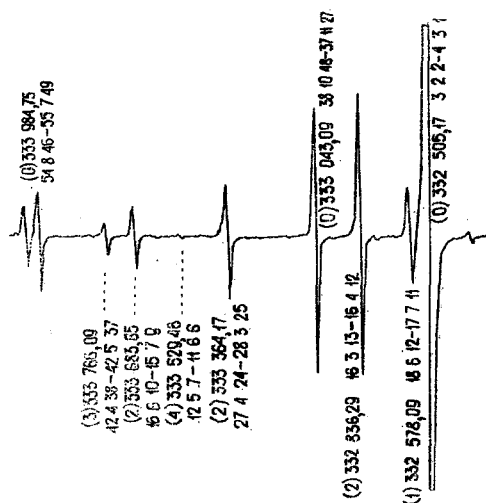


Fig. 1

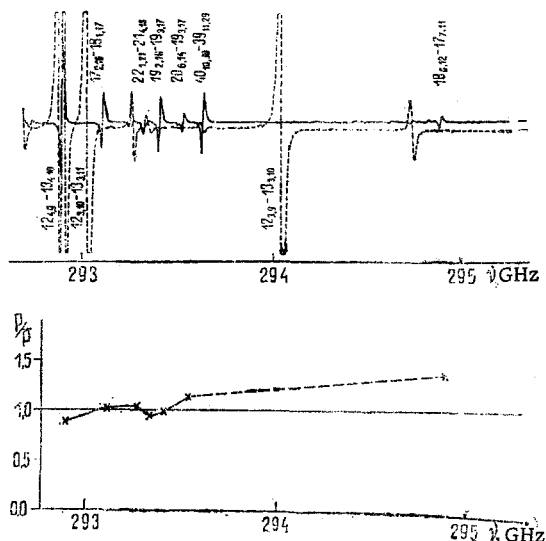


Fig. 2

Fig. 1. Sector of the reference spectrum of SO_2 . The identification and frequencies of the lines of the ground states of $\text{S}^{32}\text{O}_2^{16}$ and $\text{S}^{34}\text{O}_2^{16}$ [correspondingly, (0) and (2)] are indicated, as well as the states (010), (020), (100) of $\text{S}^{32}\text{O}_2^{16}$ (1), (3), (4).

Fig. 2. Sector of simultaneous recording of the spectra of acetic acid HCOOH (dashed line) and sulfur dioxide SO_2 (solid line). The bottom part of the figure shows a graph of the dependence of the BWT power (in relative units) on frequency which was plotted according to the lines of the SO_2 spectrum.

3. In order to perform the measurements two RAD cells placed in tandem along the path of the submillimeter radiation from the BWT are filled — one with the investigated gas and the other with SO_2 . Frequency scanning of the BWT allows two spectra to be recorded synchronously with respect to frequency on the tape of the two-pen automatic recorder: the investigated and reference spectra. A sector of such a recording is displayed in Fig. 2.

a) Measurement of the frequencies of the spectral lines of the investigated gas is performed by interpolating the dependence of the BWT frequency on time (or on the running coordinate on the tape with the recording) according to the known frequencies of the reference spectrum. The accuracy of the measurements was estimated by comparing the frequencies of the spectral lines of formic acid (HCOOH) which are determined from the reference spectrum with the results of control measurements whose relative accuracy is better than $3 \cdot 10^{-6}$ (viz., Table 1) and also with the results of handling the experimental frequencies of the rotational spectrum of HCOOH within the framework of the nonrigid-asymmetrical-top model. In the handling process the following were used: the frequencies of 50 HCOOH lines in the 265–325 GHz range, measured from the reference spectrum; the frequencies of 20 lines in the 313–472 GHz range obtained from control measurements by comparison with the harmonics of a quartz oscillator; the frequencies of 66 lines in the 22–202 GHz range which were given in [4]. The mean-square deviation of the results of the measurements relative to the reference spectrum which was estimated in this manner amounts to 14 MHz, which yields a relative error of $4 \cdot 10^{-5}$ at a frequency of 300 GHz.

b) The relationship between the power produced by the coherent-radiation generator at the frequencies of the reference-spectrum lines (ν_1 and ν_2) can easily be obtained by comparing the experimental and theoretical intensity ratio of the chosen reference lines. Actually, it follows from (1) for $\gamma_l \ll 1$ that

$$\frac{A_1}{A_2} \frac{\gamma_2}{\gamma_1} = \frac{P(\nu_1)}{P(\nu_2)}. \quad (2)$$

The quantity γ_2/γ_1 may be calculated for the rotational spectra of the molecules. This allows the intensity ratios A_1/A_2 of the lines measured on the recording of the spectrum to be used in order to determine the dependence of the radiation power in relative units on the frequency at a large number of points over the frequency range (Fig. 2). The results of applying the expounded method to an investigation of the principal source of coherent radiation in the submillimeter range (the BWT) are given in [5]. The absolute calibration of the power graph may be performed at one of the points in a range which is such that it contains the

TABLE 1

Identification of the lines	$\nu_1 \pm 14, \text{MHz}$	$\nu_2 \pm \Delta, \text{MHz}$	$\nu_1 - \nu_2, \text{MHz}$
$13_{12,2} - 14_{12,3}$ $13_{12,1} - 14_{12,2}$	314988	$314994,5 \pm 0,8$	- 6,5
$13_{6,7} - 14_{6,8}$ $13_{6,8} - 14_{6,9}$	315040	$315041,6 \pm 0,1$	- 1,6
$13_{5,8} - 14_{5,9}$ $13_{5,9} - 14_{5,10}$	315197	$315197,9 \pm 0,8$	- 0,9
$13_{4,10} - 14_{4,11}$	315497	$315495,3 \pm 0,8$	+ 1,7
$13_{4,9} - 14_{4,10}$	315568	$315559,3 \pm 0,1$	+ 8,7
$13_{3,11} - 14_{3,12}$	315634	$315621,0 \pm 0,1$	+13,0
$13_{3,10} - 14_{3,11}$	317086	$317077,2 \pm 0,1$	+ 8,8
$13_{1,12} - 14_{1,13}$	321782	$321783,6 \pm 0,1$	- 1,6
$13_{2,11} - 14_{2,12}$	323058	$323059,7 \pm 0,1$	- 1,7

Note. Frequencies of the spectral lines of HCOOH , which were determined from the reference spectrum (ν_1) and in the control measurements (ν_2).

absorption lines of the gas and provides the possibility of measuring the power in absolute units (for example, in the centimeter range). It should be noted that the weak effect of the cell with the gas on the transmitted power allows a transmitted-power meter to be created for continuous monitoring.

c) In order to measure the absorption coefficients of the spectral lines in relative units, the dependence of the BWT power on frequency [item b)] is first of all determined from the reference spectrum; then, since the cells are penetrated by the same radiation flux, it follows that by means of (2) one can easily obtain the ratio γ_1 / γ_2 for the lines of the investigated spectrum. The following method is very convenient for absolute calibration: both cells are filled with the investigated gas, and the recording is performed from the second cell under the condition that the width of the line in it is considerably greater than in the first cell. In this case, the absorption of power in the first cell causes a dip in the center of the recorded line, and

$$\gamma = \frac{1}{l} \ln \frac{A_1}{A_2}, \quad (3)$$

where A_1 and A_2 are the signals at the output of the spectroscope which correspond to the maximum and center of the line. Figure 3 displays a recording of the absorption line of formaldehyde (H_2CO) $3_{1,3}-4_{1,4}$, which has a dip in the center, in the form of the derivative of its contour. The absorption coefficient determined from the recording is $\gamma \approx 5.9 \cdot 10^{-2} \text{ cm}^{-1}$.

It is very important that the expounded methods of measurement be based on simple handling of the recording of the spectrum obtained for single continuous passage through the frequency range (i.e., they do not require "piece" work with the spectral lines with the submillimeter equipment turned on). The tape of the automatic pen recorder is not difficult to replace by punched tape for convenience of inputting to an electronic computer for purposes of complete automation of the handling process.

4. The accuracy with which the frequency of certain lines may be measured with respect to the reference spectrum may be increased to $1 \cdot 10^{-6}$ by means of high-frequency modulation of the BWT [6]. The radiation frequency (ν_0) of the BWT is stabilized by the method described in [7] relative to the known spectral line of a gas situated in one of the two RAD cells, and then it is modulated by oscillations from an auxiliary oscillator at the frequency ν_{mod} which is controlled from several to hundreds of megahertz. Under these conditions, sideband components having the frequencies

$$\nu = \nu_0 \pm n \nu_{\text{mod}} \quad (4)$$

TABLE 2

N ₂ O line	Frequency of the line (ν_0), MHz	Modulation frequency (ν_{mod}), MHz	Expression for ν (SO ₂)	ν (SO ₂), MHz	Theoretical value of ν (SO ₂), MHz
$J = 11 - 12$ (000) [s]	301442,63	151,3	$\nu_0 + 3 \nu_{\text{mod}}$	301896,6	301896,57
		226,9	$\nu_0 + 2 \nu_{\text{mod}}$	301896,5	
$J = 11 - 12$ (01 ^{1c} 0) [s]	302131,72	235,4	$\nu_0 - \nu_{\text{mod}}$	301896,3	

Note. Frequency of the 19_{1,19}-19_{2,18} line in the rotational spectrum of the S³²O₂¹⁶ molecule, measured from the reference lines of N₂O by the method of frequency modulation of a BWT.

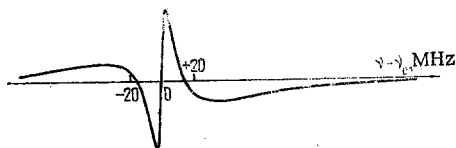


Fig. 3. Recording in the form of the derivative of the absorption line of formaldehyde H₂CO 3_{1,3}-4_{1,4} having a dip in its center (T ≈ 300 K; $\nu_0 = 281526.9$ MHz).

and a power sufficient to observe the spectral lines* appear in the oscillation spectrum of the BWT. For tuning of the frequency of the auxiliary source which plays the role of an interpolator, sectors of the spectrum of the investigated gas situated in the other RAD cell are recorded within the limits $\nu_0 \pm 0.5$ GHz. The frequency of the auxiliary oscillator was measured by an electron-counting frequency meter, frequency markers were made on the spectrum recording, and the difference frequency between the investigated and reference lines was determined within fractions of a megahertz. Table 2 displays the results of measuring the frequency of the 19_{1,19}-19_{2,18} line in the spectrum of the SO₂ molecule according to the known lines $J = 11-12$ of nitrous oxide (N₂¹⁴O¹⁶) in the (000) and (01^{1c}0) states for various numbers of sideband components. Agreement of the results with each other and with the computation lies within the limits of 0.3 MHz, which at a frequency 300 GHz yields a relative accuracy $1 \cdot 10^{-6}$. The shortcomings of the method are: complication of the observed spectrum, and boundedness of the frequency interpolation interval (± 0.5 GHz near the reference line) which reduces the number of lines whose frequencies may be measured.

The expounded results demonstrate the practical feasibility of both the rotational spectrum of SO₂ and of the procedures developed for measurement of the frequencies and intensities of large files of spectral lines in the submillimeter range. A broad field of application of the reference-spectrum method may develop in chemical and isotopic molecular analysis according to rotational spectra, where the accuracy obtained by this method is sufficient for identification of the lines of various substances, while the simplicity creates the possibility of extensive utilization. The reference-spectrum method acquires special significance in connection with the possibility of automating the process of handling the spectra by means of simultaneous recording of the investigated and reference spectra on punched tape, handling the recording on an electronic computer, and compiling tables of the investigated spectrum with measured frequencies and intensities. Recording of the investigated spectrum jointly with the reference spectrum is also a convenient method of storing information in a "library of spectra" whose creation in the submillimeter range is necessary as applications in this range develop.

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*For variation of the modulation index, we observe from one to four-five sideband components.

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