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THE ACCURACY OF MEASUREMENTS OF THE SPECTRAL-LINE FREQUENCIES IN THE STUDIES OF THE ROTATIONAL TRANSITIONS OF THE $^{16}O^{12}C^{32}S$ MOLECULE IN THE MILLIMETER AND SUBMILLIMETER WAVE RANGES

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The absolute error of determining the center frequency of the molecule spectral line during a single measurement, which is obtained by fitting the line shape to the model profile, is usually significantly smaller than the statistical spread in the frequencies of the repeated measurements. We discuss the possible causes of the systematic errors leading to an increase in the uncertainty of measurements of the line-center frequency. For an example of the multiple spectral measurements of the rotational transitions of the $^{16}O^{12}C^{32}S$ *molecule in the millimeter- and submillimeter-wave ranges (with a frequency of up to* 522 *GHz), by the Lamb-dip method, we determine the absolute error of the performed measurements, which amounts to* 0.4 *kHz. New precision values of the center frequencies of the rotational transitions of the* $^{16}O^{12}C^{32}S$ *molecule and more accurate values of the rotational constants, which are calculated using the measured frequencies, are presented.*

1. INTRODUCTION

At present, obtaining precision laboratory values for the frequencies of the molecular transitions and studying their hyperfine structure is a topical problem. This problem is important for the ground- and space-based radio astronomy, as well as conducting fundamental astrophysical and spectroscopic studies [1, 2]. An absolute error of the astrophysical measurements of the frequencies of the gas-molecule spectral lines (especially in dark interstellar clouds, where the temperature is about 10 K and lower) reaches 1 kHz [3–5], which is about an order of magnitude lower than the absolute error 30–100 kHz of the laboratory measurements (without the Doppler-effect shift) of the frequencies of most molecular lines in the millimeter-wave range.

It is also known that the error of determining the spectral-line center frequency from the microwave measurements using the method of matching the experimental line shape (most frequently, the Doppler and Lorentz profiles) with the model profile can only be a few hertz. The statistical error of determining the line-center frequency using this method is written as [6]

$$S_{\Delta\nu} = K(\Delta\nu\,\Delta\nu_{\rm dig})^{1/2}\,\Delta A/A, \tag{1}$$

where K is the coefficient dependent on the line shape ($K \approx 1.4$ and $K \approx 3$ for the Doppler and Lorentz profiles, respectively), $\Delta\nu$ is the half width of the line at its half maximum, $\Delta\nu_{\rm dig}$ is the frequency step

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for the digital record of the line, A is the signal amplitude at the line center, and ΔA is the standard deviation of the experimental data from the model profile of the line, which is called the residual. Therefore, for 1000 dots per line, the ratio $\Delta A/A \approx 1000$ (usually this ratio is equal to the signal-to-noise ratio), and the Doppler linewidth $\Delta\nu_{\mathrm{D}} \approx 1$ MHz, which is typical of the submillimeter-wave range, the error of determining the line-center frequency according to Eq. (1) does not exceed 100 Hz. As was mentioned above, the actual measurement error is as a rule tens of kilohertz. Therefore, it is necessary to clarify the cause of such a significant discrepancy between the theoretical and experimental values of the absolute measurement error, as well as find the actually achievable errors (relative and absolute) when measuring the spectral-line frequencies by the microwave-spectroscopy methods.

It should be noted that Eq. (1) gives only an estimate of the statistical measurement error, which can be obtained during a single recording of the line profile. In spectroscopy, it is assumed that the actual experimental error in measuring the line frequency is about 1/20 of the measured linewidth. This is related to the fact that the experiment involves systematic-error sources, e.g., the drift of the measuring-equipment parameters, the presence of which is not determined explicitly. It is difficult to estimate their contribution, especially using the measurements of the frequencies of individual independent lines. Therefore, to improve the line-frequency measurement accuracy according to Eq. (1), we should first obtain a spectral line with a minimum width and a sufficiently good signal-to-noise ratio. However, the minimum achievable linewidth in linear spectroscopy is limited by the homogeneous line broadening, which is determined by the particle collisions and by the Doppler broadening in the limit [7] due to the thermal spread in the particle velocities. The microwave beam spectrometers, which employ a monokinetic molecular beam (molecules of the same energy) are perfect for the precision frequency measurements. Because of the significant suppression of the mechanisms of the Doppler line broadening, the resolution of such spectrometers attains 100 Hz [8]. But such devices are fairly complex and, usually, their frequency range is significantly restricted.

The nonlinear-spectroscopy methods [9, 10] allow one to obtain narrow lines (dips) in the Doppler profile such that the spectrometer resolution under room temperature can be improved by over two orders of magnitude. A further increase in the frequency resolution without the signal-power loss is possible by increasing the spectrometer-cell diameter and the beam width [11].

In this work, we use a sub-Doppler direct-absorption microwave spectrometer [12] with the backward-wave oscillator (BWO) as a radiation source. The spectrometer allows us to obtain resonance exactly at the spectral-line center as a result of the population saturation of the molecule-transition levels by the counterpropagating waves. In this case, a narrow dip (Lamb dip) is formed at the Doppler-profile top and the width and depth of this dip are functions of the gas pressure in the cell, the radiation flux, the ratio of the intensities of the counterpropagating waves, and some other factors.

In molecular spectroscopy, the measurement error can be determined from fitting the spectral form of the signal for not only a single line, but also all the measured lines of the molecule rotational spectrum, i.e., fitting the preliminary known theoretical model of the molecule energy levels, to the experiment by varying the independent parameters of this model. The standard deviation of the measured frequencies of a large number of lines from their values, which are calculated within the framework of the theoretical model, more accurately characterizes the experimentally achieved measurement error. The fact is that some systematic measurement errors are not found if only one line is measured, but can be determined when fitting the entire set of the line frequencies as a whole.

To ensure reliable estimation of the measurement error of the spectral-line frequencies, we performed comparative measurements of the frequencies of the rotational transitions of the $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ molecule in the millimeter- and submillimeter-wave ranges, which were carried out by the authors of this work [12, 13] and by other researchers many times (see references in [13]). This molecule is convenient for a study, because its rotational spectrum with a step of 12 GHz is well described within the framework of a simple model of the rigid rotor with only three variable parameters, while a large dipole moment, which is equal to 0.71 D [14], allows one to easily obtain narrow Lamb dips at the spectral-line centers. In addition, the rotational transitions of this molecule have no internal hyperfine structure since the nuclear spin of the main isotopes of the oxygen, carbon, and sulfur atoms is equal to zero. The above-mentioned molecule does not show the collisional line shift in response to variations in the gas pressure in a cell [15], which simplifies the measurements and improves their repeatability.

In this work, we briefly describe the experimental setup and the measurement technique and consider the causes of possible inaccuracies and systematic errors when measuring the center frequencies of the lines. The results of new precision measurements of the center frequencies of the rotational transitions of the OCS molecule in the millimeter- and submillimeter-wave ranges by the Lamb-dip method are presented. The rotational constants are determined using the measured frequency set and comparison with other works is performed. The absolute error in measuring the line-center frequencies was below 0.4 kHz.

2. THE METHOD FOR MEASURING THE FREQUENCIES OF THE SPECTRAL LINES AND ITS ERROR

A detailed description of a sub-Doppler direct-absorption microwave spectrometer with a BWO as a radiation source is given in [12]. The spectrometer employs the effect of nonlinear saturation of the spectral transitions in counterpropagating waves (the Lamb-dip method) [9, 10]. The BWO signal coherence is ensured by the phase-lock loop (PLL) [16] using the frequency harmonics of the output signal from the multiplying circuit of a PTS-6400 reference synthesizer. The BWO output radiation frequency and its absolute accuracy and stability primarily depend on the accuracy and stability of the frequency ν of the rubidium-standard signal whose data-sheet long-term frequency stability values amount to $\Delta\nu/\nu \approx (1\text{–}3) \cdot 10^{-12}$, where ν is the radiation frequency. During the measurements, the spectral width of the BWO-radiation line did not exceed 10 Hz (e.g., see the spectrum measurements for a BWO with the PLL [17]).

As the radiation passes through an absorbing gas layer with thickness L (the experimental cell length and diameter were $L_0 = 200$ cm and 11 cm, respectively), the radiation intensity $I(\nu)$ decreases according to the Beer–Lambert–Bouguer exponential law:

$$I(\nu) = I_0(\nu - \nu_0) \exp[-\alpha(\nu - \nu_0)L], \tag{2}$$

where $I_0(\nu - \nu_0)$ is the incident-radiation intensity, which can generally be a function of frequency, $\alpha(\nu - \nu_0)$ is the absorption coefficient in a gas due to the considered transition, and ν_0 is the line-center frequency. In the case of a small optical thickness ($\alpha(0)L \ll 1$), the radiation that arrives at the detector can be written as

$$I(\nu) = I'_0(\nu - \nu_0)\,[1 - \alpha(\nu - \nu_0)L], \tag{3}$$

where $I'_0(\nu - \nu_0)$ is the signal intensity of the so-called base line. The dependence of the absorption coefficient $\alpha(\nu - \nu_0)$ on the radiation frequency is determined by both the collisions of the absorbing molecules (Lorentz profile) and their thermal motion (Doppler profile), and is generally given by the convolution of these profiles, or the Voigt profile [7].

As was mentioned above, to improve the measurement accuracy for the line-center frequency, i.e., obtain narrower lines compared with the Doppler ones, the Lamb-dip method was used. Although the profile of the line with the Lamb dip generally has a fairly complex shape [18], in many cases it can satisfactorily be described within the framework of the model of decreasing the absorption coefficient at the Doppler-line maximum, which has the Lorentz profile.

To increase the signal-to-noise ratio and improve the frequency contrast of the recorded lines, the frequency (phase) modulation is used. During the demodulation, the signal is proportional to the frequency derivative of the absorption variation. Therefore, the recorded amplitude of the spectral line turns out to be much greater than the base-line amplitude. We use the sinusoidal law of the frequency variation of the radiation source whose instantaneous frequency $\nu(t)$ can be written as

$$\nu(t) = \nu - \nu_0 + \Delta \sin(\Omega t), \tag{4}$$

where t is the time, Ω is the modulation frequency, and Δ is the frequency deviation. The subsequent demodulation of the signal from the radiation detector is performed using a synchronous amplifier such that the absorption line is the frequency discriminator. To obtain a symmetric line with respect to its center and a further decrease in the base-line influence, reception at the second harmonic of the modulation-frequency, i.e., the frequency 2Ω, was used. For a small frequency deviation compared with the half linewidth $\Delta\nu_{\mathrm{L}}$ (i.e., $\Delta/\Delta\nu_{\mathrm{L}} \ll 1$ and $\Omega/\Delta\nu_{\mathrm{L}} \ll 1$), the response value is proportional to the second derivative of the line profile. The recorded line shape becomes more complex with increasing deviation and modulation frequency [18–20].

Let us consider some basic causes leading to the errors when measuring the spectral-line center frequency:

1. The line-center shift because of the finite gas pressure (as well as the Stark and Zeeman shifts). 2. Spectral-line overlapping. 3. Low signal-to-noise ratio and the presence of the "non-noise" residual during the fitting of the used model profile (inadequacy of the employed line-contour model). 4. Distortion of the line profile as a result of the hardware or absorption nonlinearities. 5. The dependence of the radiation-source power on frequency. 6. Influence of the base line or the standing wave, which results from the electromagnetic-wave reflection from the channel elements. 7. Influence of the modulation method of the signal reception on the line shape. 8. An additional line distortion because of the arrival of the neighbor modulation harmonics at the receiving channel during the frequency modulation. 9. Interference of a signal and the uncontrolled radiation coming to the detector without passing through the cell with the studied material. 10. Influence of the radiation-frequency retuning rate. 11. Uncontrolled drifts of the measurement parameters, the temperature, the working-gas pressure, and the radiation-source power. 12. Accuracy of the reference frequency standard.

The influence of the first two factors is eliminated by choosing a suitable substance. In the case considered, we used an OCS molecule having separated lines without internal structure, for which no pronounced pressure shifts were observed.

A high signal-to-noise ratio in the direct-absorption spectrometers is primarily due to the radiation power and phase noise of the source, the receiving-detector sensitivity, and the relative absorption value at the spectral-line frequency, which is determined by the line intensity and the absorbing-cell length. The power increase is not always possible since it leads to the nonlinear broadening and distortion of the line. Therefore, during the experiment, one should choose an optimal power for each line, i.e., decrease the power to obtain a narrower line without a significant deterioration of the signal-to-noise ratio. This condition imposes special requirements to the spectrum of the reference oscillator (it should have low phase noise) and the quality of the BWO PLL.

It should also be ensured that the chosen model of the spectral-contour processing meets the experimental conditions since the model inadequacy leads to significant systematic errors in determining the main parameters of the line (i.e., its intensity, center, and width). The effects leading to the line asymmetry [21], which are not always adequately allowed for in the chosen model of the line-shape fitting and, thus, result in the apparent shift of the line-center frequency, are the most critical ones for the line-center measurement accuracy.

For example, it is known that the BWO is characterized by the frequency dependence of the radiated power. For narrow lines, the frequency dependence of the incident radiation can be written in the form of the linear function $I_0(\nu) = I_0[1 + a_1(\nu - \nu_0)]$, where a_1 is the constant. The frequency dependence of the base-line signal is also related to the standing-wave appearance in a cell [22]. Multiple reflections from the elements of the quasioptical channel of the spectrometer lead to modulation of the effective length of an absorbing cell, which in the linear approximation is equal to $L(\nu) = L_0[1 + b(\nu - \nu_0)]$, where b is the constant. As the cell length increases, the standing-wave influence becomes stronger. Since the frequency period $\nu_{\mathrm{b}} = c/(2L_0)$ of the standing wave where c is the speed of light, decreases with increasing length, the response from the base line in the synchronous detector becomes higher for the frequency modulation. Interference of a useful signal, which is related to the line, with the radiation that arrives at the receiver apart from the cell leads to an additional frequency dependence of the received signal.

The frequency-dependence coefficients of the base-line intensity for various effects may have opposite signs and result in recording a symmetric line thereby masking the possible hardware shift of the line. To reveal the base-line influence on the spread in the obtained values of the line-center frequencies, the following method was used. The line location on the standing-wave slope was varied by displacing the receiver [12, 23], the radiation source, and the reflecting elements of the quasioptical channel, and the BWO-radiation parameters were also varied by changing the filament voltage and the BWO location in a magnetic field. The center was determined by averaging the line-center frequencies, which were obtained under various conditions (see [12, 13, 23]) and, as a result, the spread in the obtained values of the line frequency was found.

As was mentioned in [18, 21, 24], the line asymmetry can also be related to arrival to the second harmonic (with the frequency 2Ω) of the signal at the receiving channel and additional dispersion distortion of the line [18, 25]. Varying the frequency deviation, one can estimate the influence of these effects so that one can significantly reduce such line distortions by decreasing the deviation.

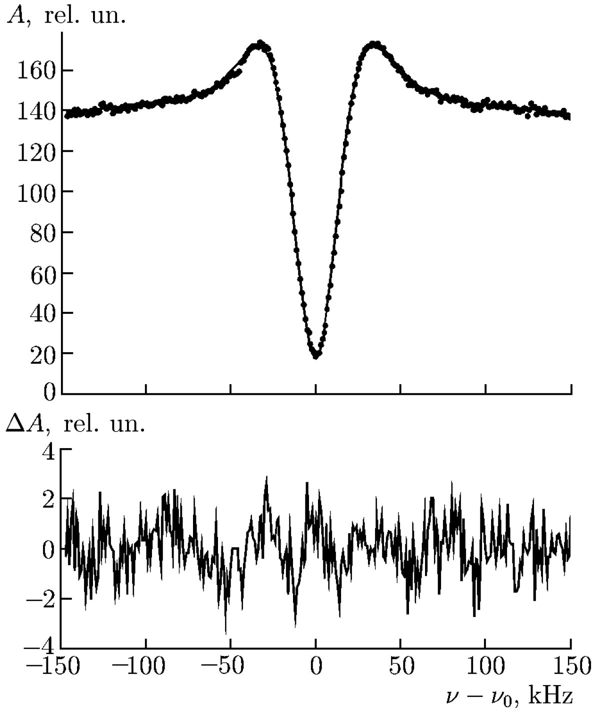

Fig. 1. On the top panel, the dots show the recorded Lamb-dip line for the frequency modulation at the $J = 43 \leftarrow 42$ rotational transition of the OCS molecule at the pressure $P < 0.4$ mTorr, whereas the solid curve shows the result of fitting the experimental data to the Voigt profile. The bottom panel shows the frequency dependence of the residual. The value of the frequency detuning Δf from the frequency (522594351.18 ± 0.04) kHz, which was determined from the fitting procedure, is indicated on the horizontal axis.

The systematic error in determining the line-center frequency because of the influence of the time constant of the receiving system was eliminated by recording the signal during the upward and downward frequency tuning at identical rates and independent processing of each record (or processing the arithmetic mean of the data of two records). The biased line-center frequency is determined as an average value over all measurements. The rate of the digital frequency tuning usually did not exceed 5 kHz/s such that the BWO-radiation phase remained unchanged. Since the value and shape of the line signal are functions of the pressure in the spectrometer cell, it should not significantly vary during the measurement time. In the case studied, the pressure variation amounted to $\Delta P = 10^{-4}$ Torr for 5–10 min.

To attain maximum accuracy in determining the line-center frequency and maximum spectrometer resolution, the measurement regime was chosen such that the Lamb-dip line is obtained with a minimum possible width and a large signal-to-noise ratio. The collisional self-broadening of the OCS-molecule lines is about 6.5 kHz/mTorr [15]. To obtain resolution above 10 kHz, the pressure in the spectrometer cell should not exceed 1 mTorr. The absorption intensity of the OCS-molecule lines at the frequencies exceeding 100 GHz and the pressure $P \approx 1$ mTorr is about $\alpha(\nu_0) \approx 10^{-3}$ cm^{-1} [14], and the optical thickness $\alpha(\nu_0)L_0 \approx 0.8$ at a frequency of 0.5 THz for the cell length $L = 2L_0 = 400$ cm. Thus, we had to decrease the pressure down to 0.1 mTorr. However, the half width at half maximum of the measured lines in our experiments exceeded the homogeneous broadening and amounted to about 15–30 kHz. The causes of the Lamb-dip broadening are discussed in [12]. Note that the main restriction imposed on the linewidth is related to the broadening due to radiation. The Rabi frequency in a beam of 10 cm in diameter amounts to $\Delta\nu_E \approx 25$ kHz for the source power 1 mW (the dipole moment 0.71 D of the molecule). Therefore, to improve the spectrometer resolution, we reduced the power and, hence, the signal-to-noise ratio.

Figure 1 shows the Lamb-dip record for the $J = 43 \leftarrow 42$ rotational transition, where J is the quantum rotational number of the OCS molecule. When fitting the line by the least-square method, we used the model function

$$I(\nu - \nu_0) = a_0[1 + a_1(\nu - \nu_0)] \exp\{-\alpha(\nu - \nu_0)L_0[1 + a_2(\nu - \nu_0)]\} + a_3(\nu - \nu_0) + a_4, \qquad (5)$$

where a_n and $n = 1, \ldots, 4$ are the coefficients reflecting the frequency dependence of the base-line intensity and $\alpha(\nu - \nu_0)$ is the absorption coefficient for a Doppler line with the Lamb dip. The center frequency of this single line record, which was obtained by fitting this model profile (eight free parameters were used), was equal to (522594351.18 ± 0.04) kHz and the error was only about 40 Hz. The estimated error in determining the line-center frequency from Eq. (1) yields a close value (about 35 Hz for $K \approx 1$), whereas the statistical spread over several measurements of this line is about 1.2 kHz.

Figures 2 and 3 show the results of multiple measurements of the line-center frequencies of the OCS-molecule rotational transitions $J = 28 \leftarrow 27$ and $J = 33 \leftarrow 32$. Obviously, the spread in values is about 1 kHz in one case and 0.2 kHz in the other case, respectively, i.e., significantly exceeds the line-frequency determination error for single measurements, which is about 50 Hz. Therefore, the actual measurement accuracy is much worse than it follows from Eq. (1). The quality discrepancy of the experimental data shown in Figs. 2 and 3 is related to the fact that in the latter case, we used experience gained in the process of choosing the most optimal measurement technique and tuning the appropriate spectrometer equipment.

3. DISCUSSION OF THE MEASUREMENT RESULTS FOR THE ^{16}O^{12}C^{32}S MOLECULE LINES

Although the multiple-measurement procedure requires long time, it allows one to evaluate possible systematic errors, as well as to eliminate them and improve the measurement accuracy. The statistical error of the repeated measurements should tend to the single-measurement error, which is determined by Eq. (1). This is a criterion of absence of the uncontrolled factors leading to the measurement errors, but is not a criterion of that the absolute error is equal to the statistical one, which is obtained from fitting the line profile. The absolute error can be estimated only from the comparative experiments, e.g., those performed in different laboratories by different techniques, as well as by comparing with the spectral-line frequencies of other molecules and analyzing the results of global fitting of the lines that are measured in a wide frequency range.

We measured the OCS-molecule lines for several years within the framework of the spectrometer tests, i.e., the frequencies of these lines were used as the secondary frequency standards. The measured frequencies were compared with those given in [13]. As a result of the repeated experimental tests, we obtained a more accurate data set compared with that presented in [13]. A typical spread in the values of the measured frequencies of the OCS-molecule rotational transitions in the range 40–500 GHz usually did not exceed 1 kHz.

The fact that the measurement error for the spectrometer [12] used in this work is lower than that presented in [13] is confirmed by an example of the test measurements for the CO molecule whose lines were also recorded many times and used for additional tests. The maximum frequency spread according to the data of 38 independent measurements of the line-center frequency ($J = 3 \leftarrow 2$) in [12] for the CO molecule (Fig. 5 in [12]), which were performed on different days with three different reference synthesizers in the spectrometer and with different PLL configurations, amounted to about 1.5 kHz. However, the spread in the center frequencies of the CO lines ($J = 4 \leftarrow 3$), which are shown in Fig. 2 in [13], was about 4 kHz. This is related to the fact that the spectrometer resolution in [13], was worse than 30–60 kHz while the base-line influence was stronger (the total length of the channel was $2L \approx 17$ m).

For the OCS triatomic linear molecule, the frequency of the $J + 1 \leftarrow J$ rotational transitions as a function of the number J, is readily determined from the model of a rigid rotor with three rotational

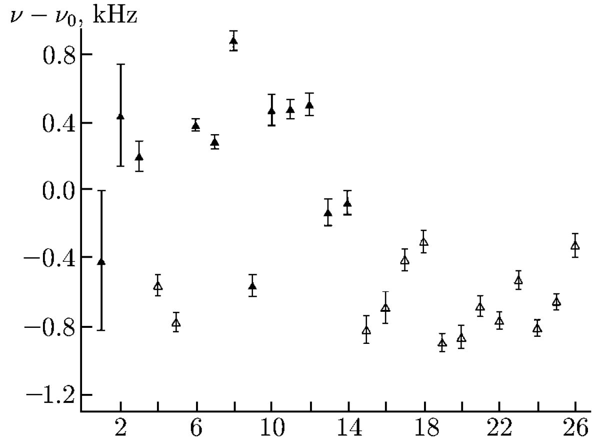

Fig. 2. The measured line-center frequency of the OCS-molecule rotational transition $J = 28 \leftarrow 27$. The transition frequency averaged over all measurements is 340449.27391(82) MHz. The measurement number is shown on the horizontal line. The vertical segments denote the confidence interval.

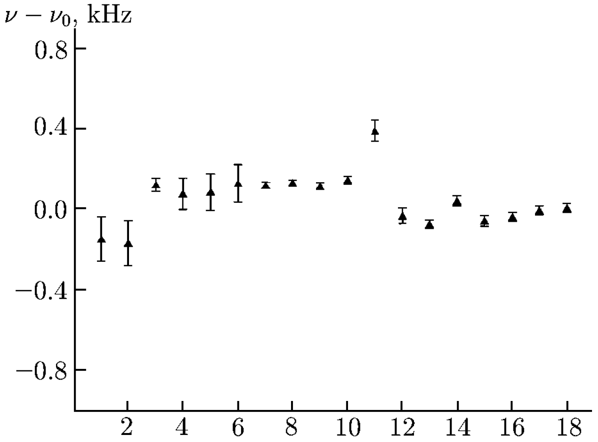

Fig. 3. The measured line-center frequency of the OCS-molecule rotational transition $J = 33 \leftarrow 32$. The transition frequency averaged over all measurements is 401191.38104(12) MHz.

constants B_0, D_0, and H_0 [26]:

$$\nu(J) = 2B_0(J+1) - 4D_0(J+1)^3 + 2H_0(J+1)^3(3J^2 + 6J + 4). \tag{6}$$

In [12], to fit the OCS-molecule spectrum and determine the rotational constants, we used the line-center frequencies of the molecule, which were obtained by the authors of this work and other workers. Using the Lamb-dip method, we obtained less than one-third of the frequency values in the range up to 1.1 THz.

In this work, only the last measurements in the range from 36 to 522 GHz, which were made by the Lamb-dip method using the spectrometer [12], and 11 frequencies near 1 THz, which were measured by us previously [13] by another method using the spectrometer with the acoustic cell [16], were used for the fitting. Although the measurements near 1 THz have a larger error (the Doppler linewidth reaches 1 MHz), they allow one to more accurately determine the constant H_0, which is required for a more exact prediction of the transition frequencies for $J > 100$. To ensure the check and a more accurate determination of the constant, the measurements for $J = 0, 1$, and 2 were also carried out using the beam spectrometers [27–29]. The constants and the corresponding frequencies were calculated using a code described in [30]. The rotational constants, which were obtained and taken from [13], are shown in Table 1.

The measured (f) and calculated (f_c) frequencies of the rotational transitions are given in Table 2. The standard deviation of the fitting is about 0.4 kHz for frequencies of up to 522 GHz (Lamb measurements) and about 9 kHz for all frequencies of up to 1.1 THz. The standard deviation for frequencies of up to 0.52 THz in [13] amounts to about 3 kHz, which is almost an order of magnitude worse than that for the described fitting. Comparing the calculated frequencies obtained by fitting in [13] with those in this work, we see that the rms difference among all frequencies is about 1.5 kHz, which exceeds the error 0.4 kHz. of the described measurements.

Therefore, the obtained frequencies of the rotational transitions of the OCS molecule and the corresponding rotational constants testify to an improvement in the measurement accuracy compared with the previous measurements [13].

TABLE 1.

Constants	This work	Work [13]
B_0, MHz	6081.4921420 (24)	6081.4921150 (52)
D_0, kHz	1.30144070 (16)	1.3014274 (32)
H_0, mHz	−0.08838 (25)	−0.08938 (33)

TABLE 2.

$J+1$	f, MHz	f_c, MHz	$f-f_\mathrm{c}$, kHz
1	12162.979(1) [27]	12162.97908(0)	−0.08
2	24325.927(1) [28]	24325.92692(1)	0.08
3	36488.8121(4) [29]	36488.81230(1)	−0.20
4	36488.812(1)	36488.81230(1)	−0.30
5	48651.6033(20)	48651.60397(2)	−0.63
...	...	...	...
7	85139.10521(54)	85139.10440(4)	0.81
8	97301.20897(26)	97301.20890(4)	0.07
9	109463.06386(17)	109463.06352(4)	0.34
10	121624.63708(18)	121624.63702(4)	0.06
11	133785.89805(15)	133785.89817(5)	−0.12
12	145946.81574(10)	145946.81572(5)	0.02
14	170267.49503(17)	170267.49508(5)	−0.05
15	182427.1944(2)	182427.19441(6)	−0.01
16	194586.42488(20)	194586.42518(6)	−0.30
17	206745.15620(15)	206745.15616(6)	0.04
18	218903.3555(8)	218903.35610(6)	−0.60
19	231060.99381(40)	231060.99375(6)	0.06
20	243218.03780(33)	243218.03788(6)	−0.08
21	255374.45714(51)	255374.45723(6)	−0.09
22	267530.22052(52)	267530.22055(6)	−0.03
23	279685.29666(59)	279685.29660(6)	0.06
24	291839.65362(80)	291839.65413(6)	−0.51
25	303993.26239(32)	303993.26188(6)	0.51
26	316146.08863(74)	316146.08859(6)	0.04
27	328298.10266(94)	328298.10303(6)	−0.37
28	340449.27391(82)	340449.27392(6)	−0.01
29	352599.57022(39)	352599.57001(7)	0.21
30	364748.96032(47)	364748.96004(7)	0.28
31	376897.41268(60)	376897.41274(7)	−0.06
32	389044.8976(11)	389044.89686(8)	0.74
33	401191.38104(12)	401191.38112(9)	−0.08
34	413336.8344(10)	413336.83426(9)	0.14
35	425481.22489(23)	425481.22500(10)	−0.11
36	437624.5221(7)	437624.52209(11)	0.01
37	449766.6936(14)	449766.69423(12)	−0.63
38	461907.71040(38)	461907.71015(13)	0.25
39	474047.5375(20)	474047.53858(14)	−1.08
40	486186.1479(23)	486186.14823(16)	−0.33

41	498323.50802(54)	498323.50782(17)	0.20
42	510459.58671(109)	510459.58606(19)	0.65
43	522594.35135(117)	522594.35166(20)	−0.31
...	...	...	...
74	897950.171(7)	897950.16026(215)	10.74
75	910026.384(11)	910026.38170(231)	2.30
76	922100.248(16)	922100.25608(248)	−18.08
76	922100.238(11)	922100.25608(248)	−8.08
77	934171.756(13)	934171.75197(267)	17.03
77	934171.769(10)	934171.75197(267)	4.03
78	946240.830(11)	946240.83796(286)	−7.96
79	958307.437(28)	958307.48261(307)	−45.61
...	...	...	...
85	1030654.359(27)	1030654.32214(460)	36.86
86	1042702.991(16)	1042702.99714(491)	−6.14
87	1054748.975(16)	1054748.97921(524)	−4.21
88	1066792.231(10)	1066792.23690(558)	−5.90
90	1090870.459(29)	1090870.45318(632)	5.82

4. CONCLUSIONS

It has been shown that the error of determining the center frequency of the molecule spectral line by a single measurement is significantly lower than the statistical spread in frequencies of the repeated measurements and, thus, is not correct. The possible causes of the systematic errors, which lead to an increase in the uncertainty of the measurements of the center frequencies, and the methods for revealing these errors have been discussed. The experimental values of the rotational-transition frequencies of the $^{16}O^{12}C^{32}S$ molecule have been obtained with an absolute error of about 0.4 kHz and the rotational constants have been determined for the range up to 522 GHz. The spectrum calculation performed using the results of processing the experimental data allows one to employ the measured and calculated line frequencies as a secondary frequency standard.

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