

## Accurate broadband rotational BWO-based spectroscopy

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### ABSTRACT

The capability, accuracy and precision of broadband spectrometers developed in the Microwave Spectroscopy Lab in Nizhny Novgorod on a basis of backward wave oscillators (BWOs) are presented. Examples of high accuracy laboratory measurements of molecular transition frequencies, shifts, and line shapes spanning many orders of magnitude in pressure are given. The importance of sensitive broadband line measurements in the millimeter and submillimeter wavelength range to both atmospheric and astronomical observations is discussed in the context of the laboratory precision and accuracy required for their interpretation. The demands on the quality of laboratory measurements have become very stringent. The present state of broadband BWO-based spectroscopy is shown to satisfy these demands. Accurate measurements are also needed for further studies of the physics of the molecules and their interactions. The capabilities and prospects for further research and development are discussed.

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### 1. Introduction

Obtaining a broad continuous spectrum record with the ability to “zoom” it around any desirable frequency is essentially an “ideal” kind of spectroscopy for an experimentalist. Historically, BWO-based spectroscopy was the first to reach the “nearest-to-ideal” condition for recording broad molecular rotational spectra throughout the entire millimeter and submillimeter ranges where the rotational spectra of most molecules are located, with the ability to obtain “zoomed” detailed records of the spectra with high sensitivity at each frequency point. One deviation from the ideal record was the necessity to use several tubes to cover the whole range mentioned. An example of part of a record of one molecular spectrum obtained using a spectrometer with an acoustic cell, and non-stabilized BWO, whose frequency was scanned only by scanning the output of a high-voltage supply, is presented in Fig. 1.

The coverage of the frequency range by a set of BWOs is comparable to the whole extent of the rotational spectrum, and the record also demonstrates the ability to observe each rotational line separately.

After recording the spectrum there is a problem of measurement accuracy. In metrology, the accuracy of measurements is defined as the degree of closeness of measured quantity to that quantity's true value [2]. The precision of a measurement, also called reproducibility or repeatability, is the degree to which re-

peated measurements under unchanged conditions show the same results. Although the two words can be synonymous in colloquial use, they are different in the context of the scientific method. For many spectroscopic applications accuracy of measurements is most important. As an example, the accuracy of knowledge of the collisional parameters of spectral lines used in remote sensing defines the accuracy of recovery of the temperature, pressure and humidity profiles of the atmosphere from satellite spectral measurements, which will be shown in more detail in what follows. Eliminating the systematic error improves accuracy. Accuracy of the measurements can be checked by comparing the measurements made by different methods with different instruments. A significant part of our efforts has been directed at increasing the accuracy of spectroscopic measurements and the development of methods to determine the accuracy. In this paper, we consider the methods of accurate measurement and examples of checking the accuracy.

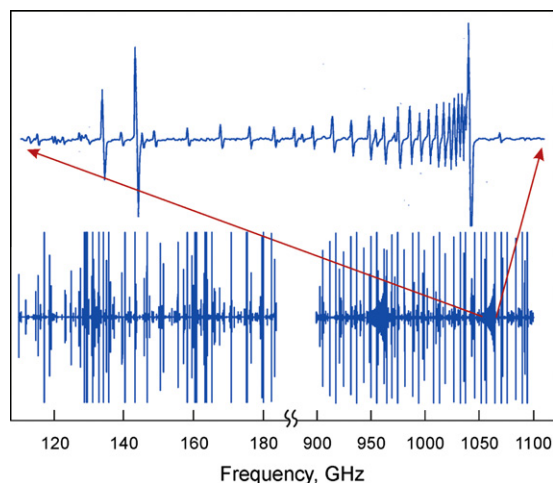
In subsequent years, the BWO-based spectroscopy technique was significantly developed, and many types of measurements by this technique define the present level of accuracy of spectroscopic measurements in the millimeter and submillimeter part of the spectrum. The general aim of the present paper is to summarize the most recent developments, descriptions of which are scattered among different journals, and present them to researchers who have an increasing need for accurate measurements for quickly developing future studies and applications. Some of the latest results are also presented.

In Section 2, we discuss the necessity of phase locking the BWO for the precise and accurate measurements, Section 3 is devoted to

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**Fig. 1.** (adapted from [1]). Parts of the rotational spectrum of the  $\text{SO}_2$  molecule. The lower panels present the spectra in the range of tubes OB-86 (left) and OB-83 (right). The upper panel is a zoomed part of the spectrum in the 1054–1066 GHz range. The spectrum is recorded by a non-stabilized BWO and a gas cell with acoustic detection of absorption.

baseline problem elimination. In Section 4, some studies with the spectrometer with radio acoustic detection of absorption (RAD spectrometer) are presented. In Section 5, some studies with the resonator spectrometer are described. Section 6 presents complementary studies by RAD and resonator spectrometers. In Section 7, the double-cavity spectrometer operations and study of the water-related continuum absorption are given. In Section 8, operation of the video spectrometer with BWO and cryogenic detector is described. In Section 9, conclusions and some prospects are presented. All Sections are united by pursuit of improvement of accuracy of spectroscopic measurements in different conditions and for different techniques.

## 2. The necessity of phase locking the BWO

The first and most natural way of obtaining a broadband and sufficiently accurate frequency scale, especially with an acoustic detection spectrometer [3], was to simultaneously record the studied and reference spectrum with two acoustic cells in series along the radiation beam. The transition frequencies of the studied spectrum are then derived by interpolating between the known lines of the reference spectrum. However, experience shows that the frequency measurement accuracy of this method is significantly limited by the irregularity of the BWO frequency dependence on the voltage applied, extending down to the smallest scale. Consequently, the accuracy of measurement of the line frequencies by interpolation between the lines of the reference spectrum were in apparent disproportion to the expected accuracy for the lines with a remarkably high signal-to-noise ratio (SNR).

Thus, it was understood that precise measurements require active high-precision BWO frequency control through the use of a phase lock loop to a precision reference, which means a “frequency synthesizer” covering the whole wavelength range of the BWO. The development of the first submillimeter BWO phase lock loop [4] was followed by more advanced systems, including (in the millimeter-wave range) commercial frequency synthesizers [5]. One of the harmonics of this synthesizer, produced by a multiplier-mixer based on a Schottky diode, served as a reference signal in submillimeter frequency synthesizers (see, for example [6]). The construction of the most widely used quasi-optical multiplier-mixer operating without tuning in the 200–1100 GHz range is

described in [7–9]. BWO frequency control was realized through a small additional voltage produced by a phase detector and video amplifier and applied to the 50–100  $\Omega$  resistor connected in series with the main high-voltage BWO supply. A broad band frequency control was carried out by simultaneous automatic adjusting the output of the high-voltage supply. This technique was used together with the absorption cell with an acoustic detector (determining the main features of the modern RAD spectrometer). A number of examples are presented below.

The development of a resonator spectrometer [10] required some modification of the frequency synthesis scheme by introducing a fast phase-continuous scan of the BWO frequency for proper resonator excitation, which was realized through the use of a radio-frequency direct digital synthesizer (DDS) as a local heterodyne at the intermediate frequency of the phase-lock loop. To extend the fast phase-continuous scan range, a digital intermediate frequency divider was employed.

Precise control of the BWO frequency is essential in the accuracy of line shape measurements. It helps eliminating the baseline problem because it makes possible recording of well reproducible spectra with and without studied sample.

A detailed description of the BWO-based synthesizers developed before 2001 for the interested reader can be found in a separate review paper entitled “Phase lock – in of mm/submm backward wave oscillators: development, evolution and applications” [8].

## 3. Baseline problem elimination

Experimental practice shows that, for precise frequency and shape measurements of spectral lines, precise frequency control is essential. Another essential point is a method of eliminating distortions produced by standing waves and/or source power variations. In the RAD spectrometer, a false signal is produced by absorption in the windows and wall surfaces of the cell; generally, it is small because of the proper choice of the modulation frequency by using the difference in the thermal inertia of the windows and walls compared with the gas sample. The acoustic detection used in the RAD spectrometer excludes the need for the radiation detector forming a cavity with the source. This eliminates the dominating standing wave, which is present in direct detection experiments. This is a huge advantage in the RAD system. Due to thermal principle of the signal formation in RAD spectrometer, the effect of the rest standing waves (reflections from windows etc.) effectively averages over the volume of the cell. The dependence of the output BWO power on frequency should also be taken into account. Output BWO power and the aforementioned false absorption signal vary with frequency much more “slowly” than the signal from the spectral lines observed. Therefore, these two effects can be taken into account by plain terms (e.g. a linear variation in power) included in the line shape model function [11]. Thus, in the RAD spectrometer, the signals from the absorption lines are recorded in the first order from the zero level, and the level of the false signals to be eliminated is small. Moreover, most of the additive “instrumental function” can be removed by a repeated record of part of the spectrum with the replacement of the sample by a gas that is not absorbing in the microwave range. Precise control of the source frequency ensures good reproducibility of records and helps to almost completely eliminate the instrumental function.

In the resonator spectrometer [10], the signal from molecular absorption is detected as a change in the resonator Q-factor, which is independent of the amplitude of the resonator response. The “baseline” in this method is represented by the inherent losses of the cavity. In an isolated resonator, the losses are smoothly

dependent on frequency. In practice, standing waves in the microwave path affect the cavity coupling loss, thus introducing changes in the resonator Q-factor. Fortunately, as in the case of RAD, the procedure of repeated recording of part of the spectrum with the gas sample replaced by a nonabsorbing gas was also successful in eliminating the baseline problem.

#### 4. Spectroscopy with the RAD spectrometer

The methodology of making accurate measurements using acoustic detection is discussed in detail in [11]. Fig. 2 shows records of relatively weak spectral lines of oxygen molecules in a range from 60 GHz to 1.12 THz obtained by the RAD spectrometer with BWO locked to a frequency synthesizer. The 11+ line of the fine structure of the  $O_2$  rotational levels at approximately 60 GHz was studied in [12]; the line belonging to the first rotational transition of  $O_2$  near 425 GHz, in [13]; and the rotational line near 1.12 THz, in [14]. The last line at 1.12 THz is the highest in frequency among the three rotational lines by which molecular oxygen was discovered by the HERSCHEL space observatory in Orion in 2011 [15]. All three oxygen lines observed by HERSCHEL were accurately studied in 2003 at our laboratory [14]. It is worth noting that the small size of the RAD spectrometer cell (1.5–2 cm in diameter and a maximum of 10 cm in length) permitted easy magnetic shielding of the cell without a loss of its sensitivity and thus eliminated the effects of the Earth's magnetic field and stray magnetic fields on the oxygen magnetic-dipole lines.

The later measurements of oxygen rotational line frequencies confirmed the high accuracy of our measurements [16].

The accuracy of the determination of the center positions of isolated lines by the RAD spectrometer with a frequency synthesizer is a few kilohertz, as shown by the examples of measurements of CO [17], OCS [18],  $O_2$  [19] and HNC [20] spectra. This level of accuracy was reached because of the high SNR and low level of the baseline and its correct account.

In addition to the line-center measurements, the collisional (pressure) broadening, shifting, and mixing parameters of the lines are measured; these measurements are very important for many applications (e.g., remote sensing) and are much more demanding. The advantages of the RAD spectrometer for such measurements are a very broad (approximately three orders of magnitude) range of operating pressures and a low baseline level in this interval. The

maximum operating pressures are higher in the RAD spectrometer than in the conventional video spectrometers in this frequency range because of the lesser effects of interference on the baseline, which permits measurements in a pressure range in which the line profile is defined predominantly by collisional broadening.

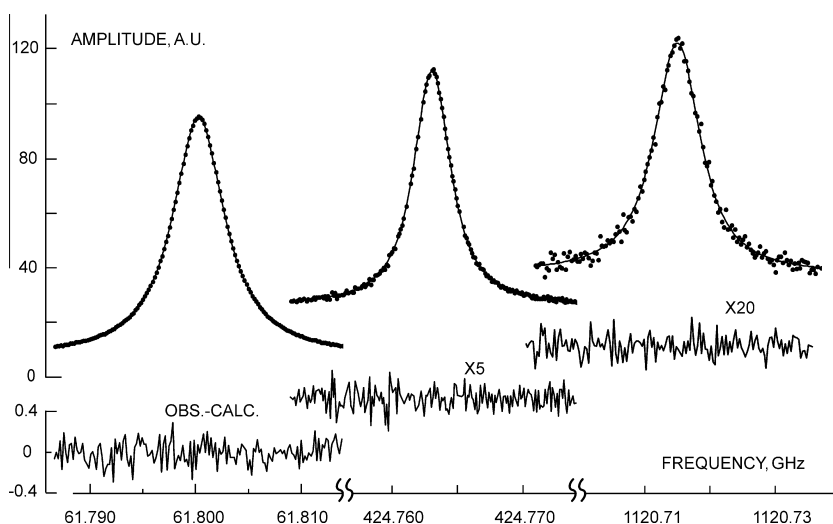
As an example, the measurements of the collisional parameters of oxygen lines reported in [12,14,19] can be mentioned. These measurements are still unique because of the difficulties with the spectroscopic study of this molecule.

Another example of accurate broadband measurements of the pressure broadening parameters is the OCS rotational spectrum study in a frequency range of 24–859 GHz, which covers almost all of the OCS rotational spectra observable at room temperature and corresponds to the interval of rotational quantum numbers  $J$  from 1 to 69.

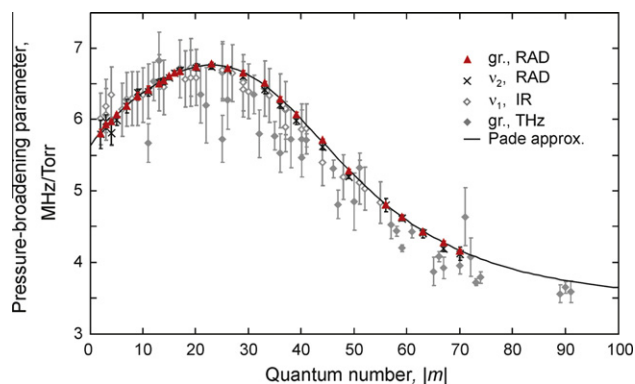
Fig. 3 shows the dependence of the OCS line pressure-broadening parameters on the rotational quantum number [18] together with the best previous THz [21] and IR [22] data. The statistical uncertainties ( $1\sigma$ ) of the pressure-broadening parameters measured and quoted in this paper lead to an average of 0.5% of the parameter value for the ground-state lines and approximately 1% for the  $v_2$  vibrational state lines. Practically, the data for rotational lines in the thermally excited  $v_2$  state served as control measurements of the ground state lines because of the prevailing rotational relaxation in the broadening that is weakly dependent on the vibrational state of the molecule. Fig. 3 also demonstrates the increased accuracy of the measurements in [18] compared with other data obtained in [21,22].

The broadening and shifting of the water line at 183 GHz, which is important for remote-sensing applications, by different perturbing molecules including the atmospheric minorities were studied using the RAD spectrometer in [23]. Figs. 4a and b demonstrates the high precision of the shifting and broadening measurements.

The broad range of pressures used in the RAD spectrometer is shown by an example of the collisional effects studied in the rotational multiplets of fluoroform ( $CF_3H$ ) in the ground vibrational state [11,24]. The multiplet shapes were studied by the RAD spectrometer at gas pressures varying by almost three orders of magnitude from  $\sim 10$  mTorr to  $\sim 10$  Torr. Fig. 5 gives a typical example of such records. It has been shown experimentally that the  $K$  components of purely rotational lines composing the multiplets exhibit no indication of collisional coupling (mixing) even at a pressure at which all components merge into a single collision-broadened profile.



**Fig. 2.** (adapted from [12–14]). Lines of the oxygen molecule (from left to right): (a) fine-structure line 11+ at 61800.157(7) MHz; (b) rotational line  $(N,J) = (3,2) - (1,2)$  at 424 763.023(2) MHz; (c) rotational line  $(N,J) = (7,6) - (5,6)$  at 1.120714836(40) THz. The RAD spectrometer with BWO locked to a frequency synthesizer was used. The obs.-calc. scale zooming factor is shown in the figure for the 425- and 1121-GHz lines.



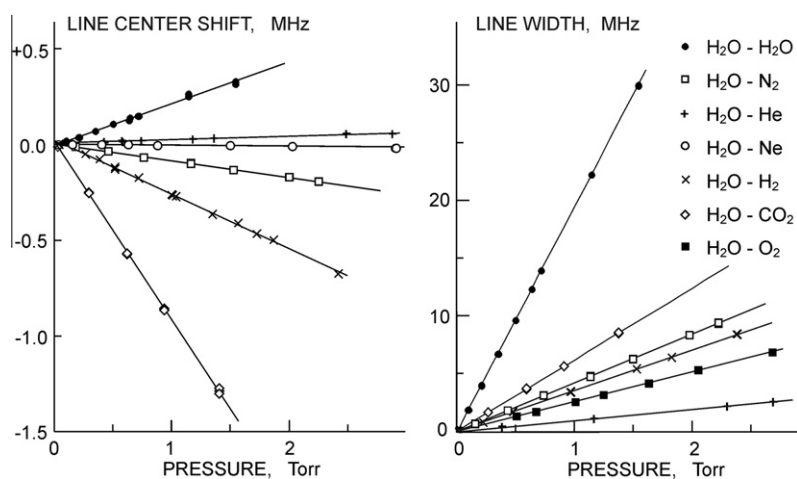
**Fig. 3.** (adapted from [18]). The OCS self-broadening parameter dependence versus the rotational quantum number at 298 K. Filled triangles and crosses are the results of measurements by the RAD spectrometer for the ground and  $v_2$  vibrational states, respectively. The  $1\text{-}\sigma$  uncertainty bars of these data are less than the symbol size. For comparison, we also show infrared data for the  $v_1$  vibrational band from [21] (open diamonds) and ground-state transition measurements by a conventional THz video spectrometer [22] (filled diamonds). The solid line is the result of the 4,4 Pade approximation for our data in the ground state.

Examples of measurements of the pressure broadening and shift of the  $1_{10}\text{--}1_{01}$  lines of different isotopomers and vibrational states of the water molecule (ground vibrational state of  $\text{H}_2^{16}\text{O}$  at

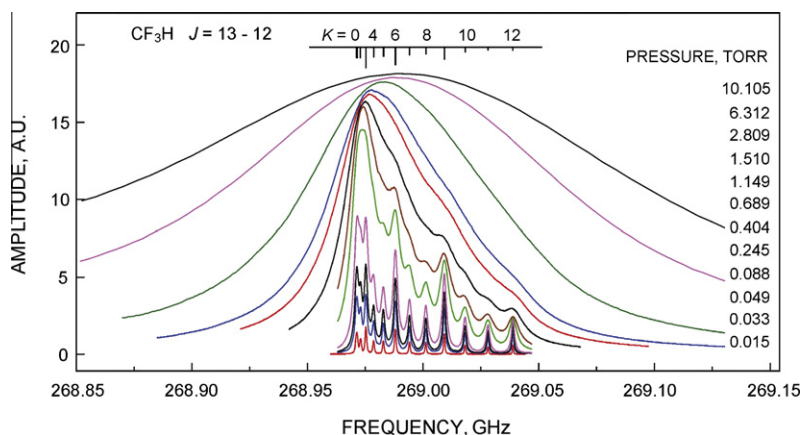
556 GHz,  $\text{H}_2^{17}\text{O}$  at 552 GHz,  $\text{H}_2^{18}\text{O}$  at 547 GHz, and the line of  $\text{H}_2^{16}\text{O}$  at 658 GHz at thermally excited vibrational state  $v_2 = 1$ ) [26] and the  $2_{11}\text{--}2_{01}$  lines of  $\text{H}_2^{16}\text{O}$  at 752 GHz,  $\text{H}_2^{17}\text{O}$  at 748 GHz, and  $\text{H}_2^{18}\text{O}$  at 745 GHz [27] show how a high sensitivity, and eliminating baseline problems increases the reliability of the measurement of these parameters by observing the same lines belonging to the different isotopic species of water of the same symmetry (in natural abundance) and/or the lines of molecules in the ground and vibrationally excited states, for which the broadening and shifting parameters are very similar in most cases. Verifying measurements of the lines that are most important for spectroscopic applications greatly improves the data reliability and confirms their accuracy.

## 5. Studies with the resonator spectrometer

The use of a BWO with another version of a frequency synthesizer, in which DDS provides a fast phase-continuous frequency scan in the resonator spectrometer, resulted in significant progress in the spectrometer sensitivity (which now reaches  $4 \times 10^{-9} \text{ cm}^{-1}$  in terms of the variation in the absorption coefficient [10]) and allowed spectral lines to be observed at atmospheric pressure. The resonator spectrometer and the RAD spectrometer are based on different principles of the spectral line signal formation. They are also different in operating pressure by approximately three orders



**Fig. 4.** (adapted from [23]). Broadening (left) and shifting (right) of the  $J_{KaKc} = 3_{13} \leftarrow 2_{20}$  line of water molecules by pressures of different gases. The data are normalized by analogy with work [25] and plotted versus partial pressure of corresponding perturbing gas. The line center shift is shown as detuning from 183.310.075 MHz.



**Fig. 5.** Evolution of the  $\text{CF}_3\text{H}$  rotational multiplet absorption with increasing pressure at room temperature.



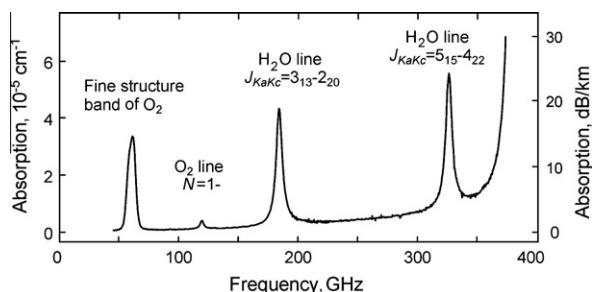


Fig. 6. (adopted from [28,29]). A resonator spectrometer record of the laboratory atmosphere absorption in the 45–370 GHz range.

of magnitude. Therefore they constitute a very useful complex of complementary instruments, which will be discussed in Section 6.

The broadband properties of a BWO made it possible to study broad (approximately 10-GHz wide) atmospheric lines at actual atmospheric conditions. The observation of broad lines in the resonator spectrometer is achieved by the measurement of the Q-factor of the consecutive longitudinal modes of the resonator (whose frequencies differ by a few hundred MHz) and thus without mechanical tuning of the resonator scanning the broad line profile “point by point.” Measuring the Q-factor is not sensitive to the source power; therefore influence of the power variations in the operating frequency range of the source can be easily excluded. Precise, fast control of the BWO frequency is used both to obtain accurate profiles of the resonances corresponding to separate modes and to switch from one longitudinal mode to another, whose position is easily predicted. The thermal stability of the resonator needs to be long relative to the measurement period for the spectrometer baseline repeatability. To provide the stability the mirror spacing rods were made of Invar alloy.

Fig. 6 presents the atmosphere absorption profile record in the 45–370 GHz range, showing the oxygen 60-GHz band, the 118-GHz single oxygen line, 183-GHz and 325-GHz water vapor lines, and the wing of the 380-GHz water vapor line [28,29]. This record is the first continuous atmosphere absorption record over such a broad frequency range. Each part of the record can be “zoomed” and studied separately in detail. As an example, detailed records of the 60-GHz oxygen band profile at different temperatures are presented in Fig. 7.

These records of the whole 60-GHz oxygen band were carried out in a frequency range of 45–85 GHz by the resonator spectrometer at atmospheric pressure and temperatures varying from  $-27.8$  to  $+60.1$  °C [30]. The large SNR together with the baseline subtraction allowed not only measurement of the first-order line coupling effects with better accuracy but also the study of the line coupling effect of the second order in pressure, whose manifestation was

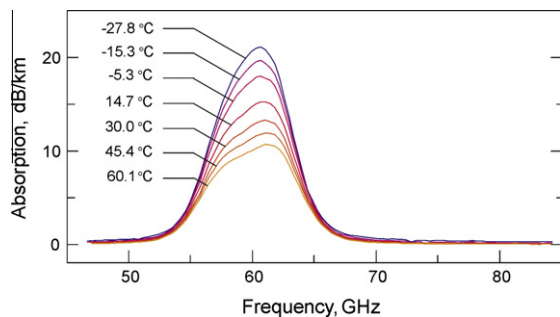


Fig. 7. (adopted from [30]). Absorption profiles of the oxygen 60-GHz band in dried atmospheric air recorded by the resonator spectrometer at several temperatures at atmospheric pressure.

found earlier in [19]. Of course, in this study, each individual line in the band was also measured at low pressures by the RAD spectrometer to obtain its precise characteristics, which were then used in the band modeling [12,19]. It is worth noting that the large sensitivity of the oxygen lines to the magnetic fields did not play a significant role at large (atmospheric) pressures. This study also allowed the experimental observation of the line coupling effect between the 118-GHz separate line and the rest of the fine structure oxygen lines for the first time [31] and confirmed experimentally the identity of the temperature dependencies of the coupling and broadening parameters. Detailed description of the resonator spectrometer and the method of measurements is given in [32].

## 6. Complementary studies

Measurements of the line parameters by two (RAD and resonator) fundamentally different spectrometers using pressures differing by up to three orders of magnitude provided a great opportunity to stringently test the reliability of the results and to estimate the relation between systematic and statistical errors in both cases.

Fig. 8 shows the results of measurements of the self-pressure line broadening of the 118-GHz oxygen line measured by the RAD (filled squares) and resonator (empty square) spectrometers (see Ref. [32] and references therein). The solid line is the result of linear regression of the RAD spectrometer points. The dashed lines show the  $1\text{-}\sigma$  statistical uncertainty of the regression. The deviation of the resonator's point from the line is shown in the inset of Fig. 8. It is astonishing that the  $300\times$  extrapolation of the low-pressure measurement falls within such a close vicinity to the result obtained by means of the resonator spectrometer at atmospheric pressure.

Similar tests were also successfully carried out for the parameters of the water vapor spectral lines (see, for example, the 183-GHz line in [29] and the 325-GHz line in [33]), which are important for applications. In both cases, low-pressure and atmospheric-pressure measurements of the pressure broadening and shifting parameters measured by the fundamentally different spectrometers coincided within experimental uncertainties. Such verification strongly confirms the reliability of the parameter values obtained and shows that, in both measurements, the systematic error coincides, in order of magnitude, with the statistical error, thus showing that the precision and the accuracy of measurements are the same.

For the line broadening measurements, stringent spectroscopic accuracy demands are dictated by analyzing error sources in remote sensing of the Earth's atmosphere. In report [34], it was noted that, if the error of assigning the broadening constant exceeds 5%, then it becomes the main error in the total error of the determination of the atmospheric parameters. Review [35] stated that “an

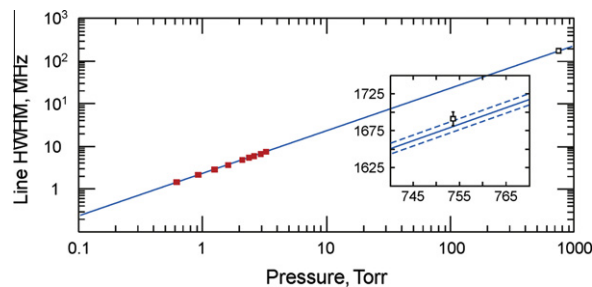


Fig. 8. (adopted from [32]). Self-pressure broadening of the 118-GHz oxygen line measured by the RAD (filled squares) and the resonator (empty square) spectrometers. See the text for details.

accuracy better than 1% is now required for adequate retrievals for several species.” Moreover, [36] stated that “an estimation of retrieval errors for the ACCURATE mission reveals that errors in spectroscopic line parameters dominate all other error sources.” Presumably, these demands on accuracy will be increasing in the future.

It is also worth mentioning a known problem in the reliability of laboratory spectroscopic measurements, which are used for interpreting remote sensing data. In [37], an insufficient number of measurements of the same parameters of water lines in different laboratories was noted: “Unfortunately, the number of inter-comparisons with  $n$  greater than 3 is small: 6%, 10%, 2%, and 0.9% for N<sub>2</sub>-, O<sub>2</sub>-, air-, and self-broadening, respectively. One rovibrational transition, the  $3_{13} \leftarrow 2_{20}$  transition of the rotational band or the 183-GHz line, was studied by seven groups, and here the estimated uncertainty is greater than 10%.” This transition of H<sub>2</sub>O was then investigated using the RAD spectrometer in [23], as was mentioned earlier, and using the two spectrometers in [29], thus resulting in an accuracy that was an order of magnitude greater than that achieved in previous studies and a reliability similar to that presented in Fig. 8 for the oxygen line.

As demonstrated above, modern requirements for accuracy and reliability of the atmospheric line parameters can be satisfied by the aforementioned methods.

## 7. The double-cavity resonator spectrometer and water-related continuum absorption study

Spectral lines at atmospheric pressure are observed on a broad continuum absorption pedestal, which must be taken into account in precise laboratory and remote-sensing measurements. However, the water-related continuum absorption measurements at atmospheric pressure posed one important problem, which was mentioned by many authors but was not resolved. This problem consists of distinguishing between the absorption in water vapor, which is the subject of interest, and the absorption in water adsorbed by elements of the spectrometer cavity, which produces a false absorption signal. A solution to this problem involved varying the optical-path length of the gas cell, keeping the rest of the radiation absorption conditions maximally the same (or unambiguously recalculated). This method was realized in the double-cavity scheme of the experiment, in which the lengths of the two resonators differ exactly by a factor of two, but the parameters of the mirrors, field structure, and coupling elements are kept the same in both resonators [32]. Such a configuration again permitted the exclusion of most of the unwanted factors affecting the measurements. Experiments show that the contribution of adsorbed water to the total measured absorption can be very significant.

Fig. 9 presents the results of the measurements of the temperature dependence of the self-continuum parameters by the conventional single-cavity method (using resonator lengths of 0.35 and 0.7 m) and by the double-cavity (length-variation) method [38]. The “true” absorption measured by the double-cavity method in the low-temperature region is several times less than the absorption measured by the single-cavity method. This difference shows the order of magnitude of the possible errors arising from neglecting the absorption by adsorbed water. With the introduction of the double-cavity method, one can obtain the “true” gas absorption values needed for proper accounting of the continuum absorption, even in the low temperature region typical for most of the atmosphere. The results of the most reliable measurements of the temperature dependencies of the measured self- and foreign-continuum parameters are presented in Fig. 10 (see Ref. 38 for more details).

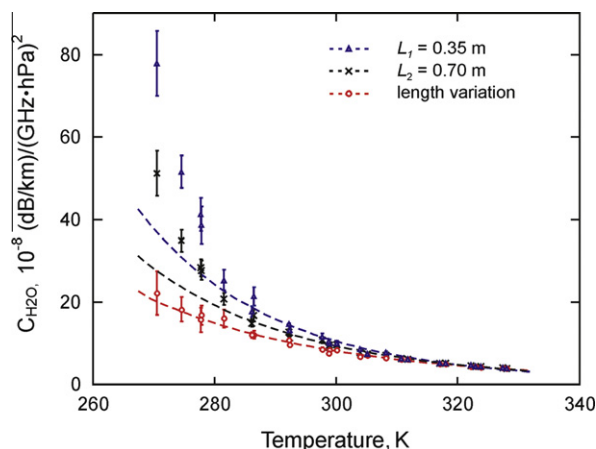


Fig. 9. (adopted from [38]). The self-continuum parameters temperature dependence obtained using one resonator at two different lengths (crosses and triangles) and by the length variation method (circles). The dashed lines are weighted fit of the power function to the data.

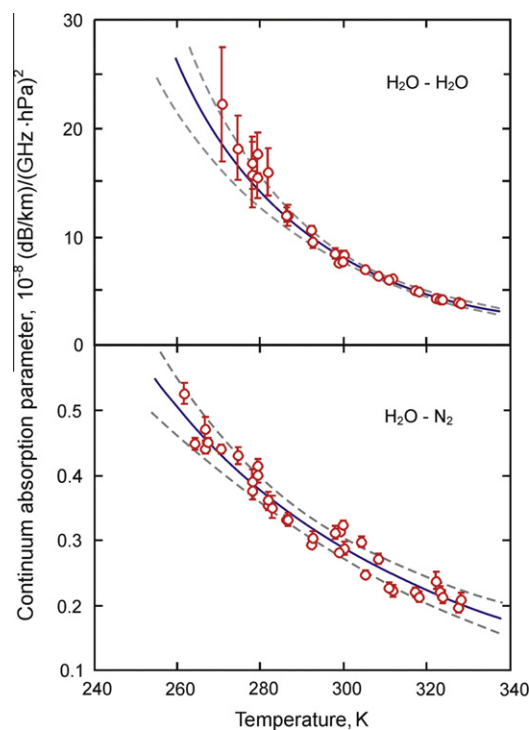
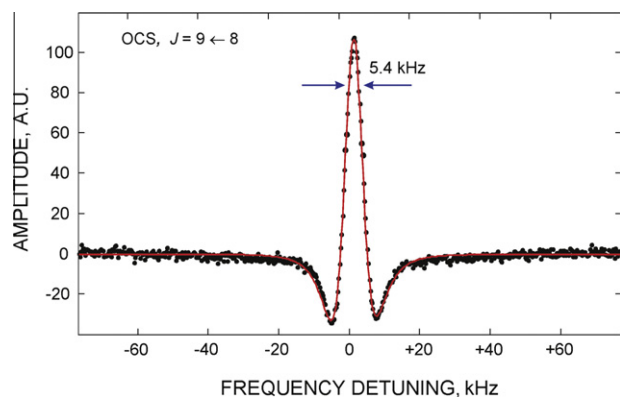


Fig. 10. (adopted from [38]). Temperature dependencies of the self- and foreign-continuum parameters, including a first-time laboratory study of the continuum at temperatures below the freezing point. The data retrieved from the experiment at fixed temperatures are marked by circles. The error bars are 1- $\sigma$  uncertainties. The solid lines are the result of a weighted fit of the commonly used power function to the experimental data. The weights were chosen as the reversed squares of the individual point uncertainty. Dashed lines are 99.99% confidence intervals.

## 8. Video spectrometer with BWO and cryogenic detector

One more BWO-based spectrometer that permits studies at lower gas pressures than in the RAD spectrometer and thus gives complementary possibilities of high- and ultrahigh-resolution research was developed by our laboratory jointly with Physical Institute of the Cologne University [7] (see also [39]) and was reproduced later in some other laboratories (see, e.g., [40]). Using this technique, many molecular spectra were explored. The regime



**Fig. 11.** Lamb dip observed in the rotational transition  $J=9 \leftarrow 8$  of the OCS molecule [42]. Frequency detuning is shown from 109463.063 MHz [41]. Collisional line width (HWHM) obtained from the fit to the Lorentz shape is 6.56(3) kHz.

required for obtaining a “Lamb dip” in a submillimeter spectrometer is described in e.g., [41]. A recent record of the line demonstrating the highest-to-date resolution for this class of spectrometers is shown in Fig. 11. This record was produced by the improved version of the apparatus currently being developed in our laboratory [42]. Narrow line improves the accuracy of measurements. Now we examine the extent of the effects of standing waves on the accuracy of measurements in this spectrometer.

## 9. Conclusions and some prospects

Broadband BWO spectroscopy achieved a new accuracy level for many kinds of measurements in rotational molecular spectra studies, as described above. The results are now included in the HITRAN database [43], the JPL Submillimeter, Millimeter, and Microwave Spectral Line Catalog [44], and the MASTER Database [45] and were employed to improve the atmospheric Millimeter-wave Propagation Model (MPM) [46,30]. The most recent use of our data [14] was in connection with the aforementioned discovery of molecular oxygen in Orion by the HERSCHEL space observatory in 2011 [15].

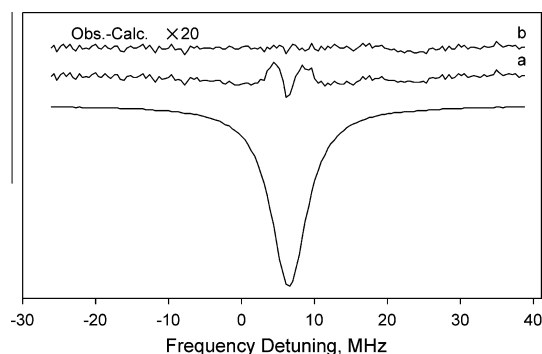
Recently, an alternative technique of spectroscopy by frequency multiplication and using cryogenic receivers progressed very rapidly, reaching frequencies near 3 THz. Among the most recent papers dealing with this technique is [47]. What can be expected in spectroscopy with primary sources? Let us consider some prospects.

First, the technique described is the basis for continuing, accurate studies of an increasing number of lines of interest in astrophysics, physics of the atmosphere, and molecular physics. In particular, the increasing number of observations of the spectral lines from modern satellites, space observatories, and high-altitude vehicles requires further laboratory measurements to support astrophysical and atmospheric interpretation of the data, which is a broad research field.

The further improvement of the accuracy of the determination of the parameters recorded with high SNR spectral lines requires the development of more accurate line-shape models than the conventional Voigt profile. Our recent study [48] shows that accounting for the dependence of the collision frequency on the relative speeds of the colliding molecules yields an adequate description of the experimental data throughout the entire operating pressure range of the RAD spectrometer. A typical example of line-shape fitting is shown in Fig. 12.

The improvement of the experiment technique is possible in several directions.

Recently, we started to develop a new-generation of mm/sub-mm synthesizers [50] with one component of the frequency comb



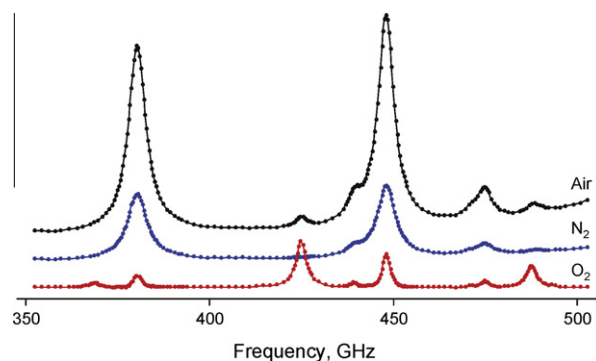
**Fig. 12.** The  $J \rightarrow J' = 58 \rightarrow 59$  line of OCS. Residuals (enlarged by 20 times) correspond to the conventional Voigt model (a) and the Speed Dependent Voigt model [49] (b). Frequency detuning is shown from 716540.0 MHz. Temperature: 297 K. Cell length: 1.5 cm. OCS pressure: 0.602 Torr. Doppler half-width at  $1/e$  level: 0.686 MHz. Voigt collisional half-width: 2.835(3) MHz.

produced by a femtosecond laser serving as a reference with the aim of significantly improving the spectrum purity of the synthesized radiation. This is especially important for the observation of narrow lines with a high signal-to-noise ratio.

In the video spectrometer, further development of a regime of the “Lamb dip” is expected, including the improvement of sensitivity and the extension of the operating frequency range.

An evident direction in the development of the resonator spectrometer is to extend measurements to the higher frequencies. An example of the continuous atmosphere spectrum recorded by the spectrometer in the 45–370 GHz range is presented in Fig. 6. Now, the operating frequency range of the resonator spectrometer based on a phase-locked BWO covers the widest range, from 45 to 500 GHz. The first continuous experimental spectrum of the laboratory atmosphere in the 350–500 GHz range recorded using a coherent radiation source [51] is presented in Fig. 13. Further extension of the spectrometer frequency range is expected.

The resonator spectrometer equipped with a vacuum chamber with controlled pressure and temperature will broaden the research capabilities. For example, the opportunity for the first observation of a resolved rotational water dimer spectrum under conditions similar to atmospheric equilibrium in the millimeter-wave range is interesting [52,53]. Similar observations in the infrared range met significant difficulties connected with the closely coinciding vibrational bands of the monomer and dimer water molecules. The subtraction of monomer lines, which is an essential procedure in dimer studies in the infrared, is unnecessary in the



**Fig. 13.** Absorption spectra of the main atmospheric gases mixed with water vapor recorded by the resonator spectrometer at atmospheric pressure and room temperature in the 350–500 GHz range. The measured by commercial sensor relative humidity of samples constitute 6.6%, 1.9% and 0% for air,  $N_2$  and  $O_2$ , respectively.



millimeter-wave range. The analysis of rigorously calculated spectrum of the dimer leads to the conclusion that the resonator spectrometer sensitivity is sufficient for observing the spectrum peculiarities corresponding to a series of rotational transitions  $J + 1 \leftarrow J$ ,  $K$  of  $E_1$  symmetry of the dimer molecules [53].<sup>1</sup>

The methods described in this paper are not limited to BWO sources only. There is, for example, another type of a tunable primary radiation source in the millimeter and submillimeter wave ranges, which is currently being developed—tunable medium power gyrotrons. Medium power in this case means a power from tens to hundreds of watts, tunability at the moment constitutes approximately 4.5% of the frequency value, and extension of the operating frequency is possible up to the terahertz region. There are also publications reporting precise (phase-lock) frequency control of these sources and their use for the solution of spectroscopic problems. The reader can be referred, for example, to [54–58]. The RAD spectrometer can directly benefit from these developments. The signal formation principle in this spectrometer suggests a drastic increase in its sensitivity with increasing radiation source power, as was mentioned in [59,60]. The use of higher-power sources also allows a new way to developing nonlinear spectroscopy, permitting, for example, observation of the rotational spectra of non-polar molecules [61,62].

Use of solid-state Terahertz radiation sources can be interesting and promising for rotational spectroscopy. Recent review paper [63] gives an overview of solid-state integrated circuit amplifiers in the submillimeter-wave range, including HEMT amplifiers. Superlattice oscillators were described recently in [64]. We did not find data about the applications of these sources for broadband rotational spectroscopy, but many groups are actively working on the development and applications of solid-state sources, and we hope for progress in these areas.

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