

Precise Measurements of Collision Parameters of Spectral Lines with a Spectrometer with Radioacoustic Detection of Absorption in the Millimeter and Submillimeter Ranges

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Abstract—The factors influencing the accuracy of determining the parameters of molecular lines with the use of a spectrometer with radioacoustic detection of absorption are analyzed. In addition, the following instrumental features of the spectrometer that were not studied earlier are analyzed: the dependence of the sensitivity of the radioacoustic cell on the pressure of the cell-filling gas and the frequency dependence of the radiation power in the cell at gas pressures lower than 10 Torr. Methods of mathematical simulation of the spectrometer's output signal at various gas pressures are considered. A technique for calibrating the dependence of the cell's sensitivity on the pressure based on measurements of the integrated absorption coefficient of molecular spectral lines is presented. With allowance for the considered features of the spectrometer, the parameters of the lines of rotational multiplet $J = 9$ of fluoroform in the ground vibrational state are studied at gas pressures of 0.01–10 Torr.

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1. INTRODUCTION

High-precision measurements of parameters of molecular spectral lines are of interest from the standpoint of both the fundamental problems of testing and developing the theory of intra- and intermolecular interactions and the solution to a number of applied problems requiring the construction of precise radiation-absorption models in gases and gaseous mixtures. At present, the development of such models—in particular, in millimeter and submillimeter wavelength ranges—is especially urgent for solving problems of satellite monitoring of the Earth and remote sounding of the atmosphere and surfaces of land and ocean. Precise values of the parameters of molecular spectral lines (MSLs) are likewise necessary for solving problems in radioastronomy, radiolocation, monitoring of technological processes, etc.

Simulation of radiation absorption in a gas at an arbitrary pressure and an arbitrary temperature requires knowledge of such parameters as the center frequency of a line, its intensity, the line shift and broadening coefficients at an increased pressure, the interference coefficient (collisional coupling of molecules), and the temperature dependences of the above parameters for all lines lying within a specified frequency range for all molecules incorporated in the gaseous mixture. The most precise method for measuring the line parameters is a regression of the simulated absorption profile containing these parameters as variable quantities to an experimental record.

A spectrometer with radioacoustic detection of absorption (RAD spectrometer) with a frequency synthesizer based on a backward-wave oscillator (BWO) used as the radiation source [1] allows investigation of the absorption profiles of MSLs in the millimeter and submillimeter wavelength ranges at gas pressures changing from tens of mTorr to tens of Torr. Owing to such a wide range of operating pressures, the RAD spectrometer is an ideal instrument for measuring collision parameters of spectral lines, primarily the pressure broadening and shift coefficients. However, there are a number of factors that affect the accuracy of the obtained data on the parameters of lines associated with specific features of both molecular absorption and the spectrometer itself.

In this paper, we present a detailed analysis of the factors that affect the accuracy of measuring the parameters of spectral lines with the RAD spectrometer, analyze the possibilities of minimizing the systematic errors caused by instrumental peculiarities of the spectrometer and affecting the shape of the observed absorption profile, and present some examples of the analysis of gas-absorption lines with allowance for these features. The possibility of using the RAD spectrometer for studying the gas absorption coefficient as a function of its pressure is demonstrated.

The information obtained in this study is used during analysis of the parameters of the rotational lines of multiplet $J = 9$ of fluoroform (CHF_3) in the ground vibrational state.

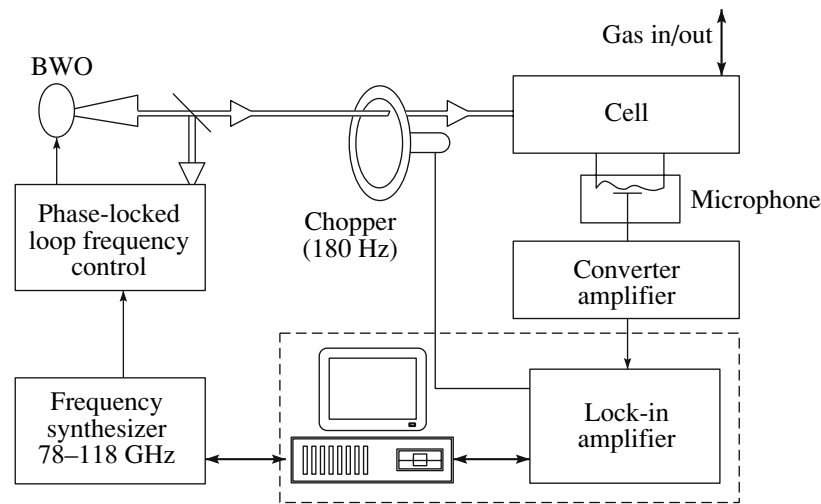


Fig. 1. Simplified block diagram of the RAD spectrometer.

2. DESIGN OF THE RAD SPECTROMETER

To reveal the instrumental features of the spectrometer affecting the shape of the observed spectral-line profile, let us briefly recollect its design and operating principle. Figure 1 shows a block diagram of the state-of-the-art version of the RAD spectrometer [2]. As the radiation source, we use a BWO the radiation frequency of which is stabilized against a harmonic of the microwave synthesizer [3] with the use of a phase-locked loop (PLL) frequency control. A radioacoustic cell filled with the studied gas serves as the detector of absorbed radiation.

The BWO-emitted radiation is interrupted by a mechanical chopper operating at a frequency of 180 Hz and directed to the cell. As the radiation is absorbed, the gas temperature and pressure change. Pressure oscillations at the modulation frequency are detected by a microphone membrane and transformed into an electric signal transferred to a digital lock-in amplifier, the output signal of which is proportional to the power absorbed in the cell and, during scanning of the radiation frequency, corresponds to the absorption profile in the gas.

Let us consider the process of formation of a radioacoustic absorption signal. Gas-absorption coefficient α is defined by the formula

$$\alpha = \frac{\Delta P/P}{\Delta L},$$

where $\Delta P = P_0 - P$, P_0 is the initial radiation power, and P is the radiation power after passage through a gas layer of thickness ΔL .

At $\Delta L \rightarrow 0$, this equality transforms into a differential equation for the radiation power propagating through the gas along the L coordinate, the solution to

which is the well-known expression called the Bouguer–Lambert–Beer law:

$$P = P_0 e^{-\alpha L}.$$

The dependence of α on the radiation frequency corresponds to the gas-absorption profile at a specified pressure.

On condition that radiation is monochromatic, the power absorbed by the gas during passage of a radioacoustic cell of length L is a function of frequency ν and gas pressure p :

$$P_{\text{abs}}(p, \nu) = P_0(\nu)(1 - e^{-\alpha(p, \nu)L}).$$

Strictly speaking, the frequency dependence of the gas-absorbed radiation power is also determined by the radiation source's spectral function $P_{\text{source}}(\nu)$, which is considered in the form of the convolution

$$P_{\text{abs}}(p, \nu) = (1 - e^{-\alpha(p, \nu)L}) \otimes P_{\text{source}}(\nu).$$

However, the use in the RAD spectrometer of microwave frequency synthesizers [3] as a source of a narrow-band reference signal and a BWO system ensures a radiation-spectrum width of <1 kHz, a value that is several orders of magnitude smaller than the linewidths observed experimentally. In addition, during step-by-step scanning of the BWO frequency in the PLL mode, the relative accuracy of frequency setting and its stability during the measurement period correspond to the stability of the reference radio signal. For an C4B-74 rubidium frequency and time standard, the relative accuracy is $\sim 10^{-11}$. This circumstance allows us not to consider the absorption-profile distortions related to both the finiteness of the width of the radiation source's spectral function and an uncertainty of the radiation frequency.

The average deflection of the microphone membrane even for the most intense spectral lines is

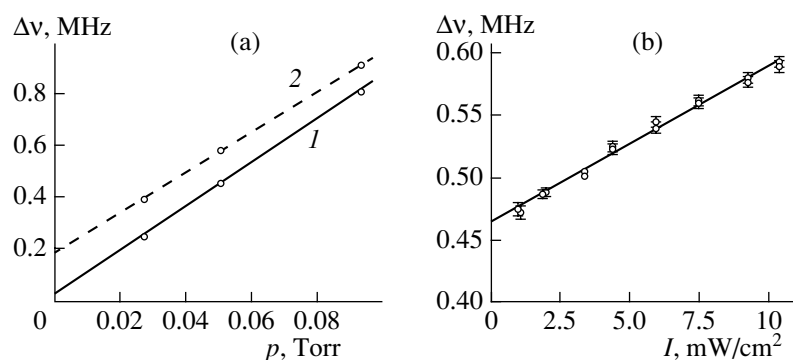


Fig. 2. Dependences of the width of the $K = 16$ line of $J = 16$ rotational multiplet of fluoroform (a) on the pressure at BWO radiation intensities of (1) 1 and (2) 10 mW/cm^2 and (b) on the BWO radiation intensity at a pressure of 0.49 Torr. Straight lines correspond to a linear regression of the measurement results shown with dots.

$\sim 10^{-7}$ cm [4], which is approximately five orders of magnitude smaller than the distance between the plates of the receiving microphone–capacitor in the cell. At such small deflections, it can be considered that a change in the capacitance of the capacitor is a linear function of the membrane displacement (the difference of the capacitance change from a linear law is 10^{-10} of the capacitance value).

Hence, the expression for the spectrometer's output signal S can be written in the form

$$S(p, \nu) = C(p)P_0(\nu)(1 - e^{-\alpha(p, \nu)L}), \quad (1)$$

where $C(p)$ is the proportionality factor depending on the transfer coefficient of receiving devices and allowing for the dependence of the sensitivity of the radioacoustic cell on the gas pressure.

The next factor that must be considered during simulation of the spectrometer signal is the low parasitic absorption of radiation in the cell's elements, which causes secondary heating of the cell-filling gas and, consequently, pressure oscillations at the modulation frequency (the phase of these oscillations differs from the phase of oscillations of the absorption signal in the gas), which are also detected by the membrane. This signal, called the instrument signal, is added together with the absorption signal in the gas. Therefore, expression (1) for the spectrometer's output signal should be complemented with an additional term:

$$S(p, \nu) = C(p)P_0(\nu)(1 - e^{-\alpha(p, \nu)L} + \beta(p, \nu)), \quad (2)$$

where $\beta(p, \nu)$ is the absorption in the cell's elements.

The mathematical expression for $\alpha(p, \nu)$ depends on the analyzed gas and the experimental conditions. For example, for an isolated spectral line in the range of operating pressures of the spectrometer, the Lorentz or Voigt functions or more precise models of the line profile, which allow for the ratios of the masses and velocities of interacting molecules [5], can be used. Unknown frequency dependences of the radiation power and instrument signal can be approximated by a

polynomial of the first or second degree depending on the experimental conditions. Hence, expression (2) becomes a model function.

The parameters of the model function are selected such that this function best corresponds to the absorption profile in the gas recorded with the spectrometer. In this case, the set of parameters allowing for the specific features of the spectrometer and the desired parameters of the studied spectral line are determined.

One of the most substantial simplifications of function (2) results from the condition that the radiation absorption is small on the length of the gas-filled cell. Most of the MSLs observed in the millimeter and submillimeter ranges have absorption coefficients $< 10^{-2}$ cm^{-1} . Therefore, for a typical length of $L = 10$ cm of the absorbing cell in the RAD spectrometer, the condition $\alpha L \ll 1$ is met almost in all cases. Then the output signal is represented in the form

$$S(p, \nu) = C(p)P_0(\nu)[\alpha(p, \nu)L + \beta(p, \nu)]. \quad (3)$$

There are several additional instrumental factors that affect the experimental absorption profile. A distortion of the line profile resulting from radiation-power-induced saturation of the transition is observed at a low pressure and a high radiation intensity in the cell. In the first approximation, this effect is displayed as additional broadening of the line profile.

Figure 2a shows the pressure dependences of the half-width of the spectral line $K = 16$ from fluoroform's multiplet $J = 16$ measured at two different intensities of 1 and 10 mW/cm^2 . These dependences have almost the same slope but intersect the ordinate axis at different points. Figure 2b shows the results of measuring the half-width of the same line at different radiation intensities and a constant gas pressure. Analysis of these dependences allows us to conclude that, at the insignificantly exhibited radiation-power effect and a constant radiation power, the power-induced broadening of the spectral line during an experiment can be taken into account in the model as a constant additive correction to the collisional linewidth.

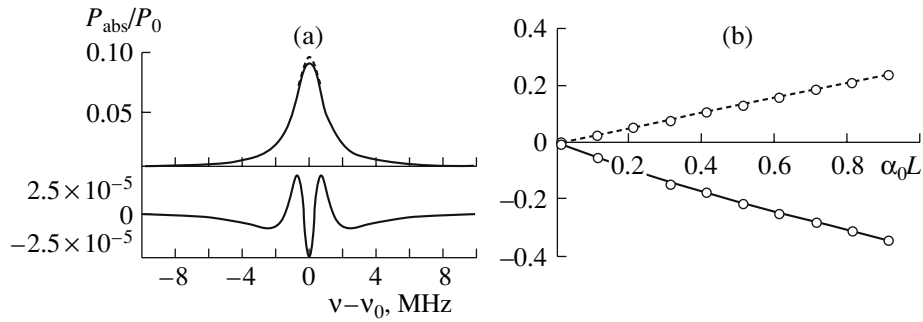


Fig. 3. (a) (Upper curves) Frequency dependence of the ratio of the gas-absorbed radiation power to the incident power—the exact absorption profile calculated according to the Bouguer–Lambert–Beer law (solid line) at $\alpha_0 L = 0.1$ and (dotted line) in a linear approximation; ((a) lower curve) residue of the regression of the model function in the form of a Lorentz profile with varied parameters of the width and amplitude to the exact absorption profile normalized to the line amplitude. (b) Systematic errors in determining the line half-width (dots connected with a dotted line) and its amplitude (dots connected with a solid line) with the use of a linear approximation of the Bouguer–Lambert–Beer law for simulating the observed absorption-line profile calculated in relative units as functions of $\alpha_0 L$ (the obtained value is normalized to the true value); α_0 is the absorption coefficient at the line center.

The next factor is the effect of molecular collisions with the cell walls, an effect that also manifests itself in an additional broadening of the spectral line [6]. As a rule, the contribution of collisions with the walls is much lower than the Doppler linewidth. However, the contribution from the walls may become appreciable if short (<1 cm) cells are used. Such cells are used for studying intense spectral lines.

If the manifestations of the aforementioned effects are insignificant, their influence on the values of the measured parameters can be considered via simulation of the corresponding distortions of the experimental profile by mathematical methods. As an example, Fig. 3 shows the calculated systematic measurement errors with the use of model function (3) provided that $\alpha L \leq 1$. However, the most reliable method is the selection of such experimental conditions under which the influence of the above effects is minimized.

Note that, under certain conditions, some unknown parameters of the model function can be determined experimentally. For example, to determine the instrument signal, the cell is filled with a gas that does not absorb radiation within the studied frequency range and has a molecular mass close to that of the gas under study (i.e., having similar acoustic properties). Then, radiation-absorption profiles are recorded at different pressures of the nonabsorbing gas. As a rule, such profiles coincide to within a constant factor depending on the pressure. This circumstance is used during consideration of the instrument signal [2]. The measurement accuracy of the parameters of a line with correct allowance for all affecting factors also depends on the signal-to-noise ratio in the experimental record of the line profile. The comparative measurements in [2, 7–9] show that, when the signal-to-noise ratio is ~ 100 , the relative error in determining the broadening coefficients with the RAD spectrometer is $\leq 2\text{--}3\%$, and the accuracy of determining the center frequencies of intense isolated lines is about several kilohertz ($\sim 10^{-8}$ rel. units).

Formula (3) shows that the RAD spectrometer does not allow measurements of the magnitude of the radiation-absorption coefficient in the gas, because the spectrometer's output signal is proportional to the radiation power at the cell input, which cannot be measured at the same mutual arrangement of the setup's elements as during recording of the absorption spectrum because of radiation interference. However, if the pressure dependence of the cell's sensitivity, $C(p)$, were known, the pressure dependence of the gas-absorption coefficient could be analyzed with the use of the spectrometer.

3. PRESSURE DEPENDENCE OF THE SENSITIVITY OF THE ACOUSTIC CELL

To analyze the pressure dependence of the gas-absorption signal, let us use simplified formula (3) and, for clarity of the expressions, ignore small instrument signal β . As a result, the spectrometer's output signal has the form

$$S(\nu, p) = P_0(\nu)\alpha(\nu, p)LC(p). \quad (4)$$

Integrating formula (4) over the entire frequency range and assuming that spectrum $\alpha(p, \nu)$ consists of a single absorption line, we obtain

$$\int_{-\infty}^{\infty} S(\nu, p)d\nu = C(p) \int_{-\infty}^{\infty} P_0(\nu)\alpha(\nu, p)Ld\nu.$$

If the dependence $P_0(\nu)$ can be approximated by a polynomial of zero or first degree in the frequency range where absorption is nonzero and the absorption-line profile is symmetric, power \bar{P}_0 can be factored outside the integral:

$$\int_{-\infty}^{\infty} S(\nu, p)d\nu = C(p)\bar{P}_0L \int_{-\infty}^{\infty} \alpha(\nu, p)d\nu. \quad (5)$$

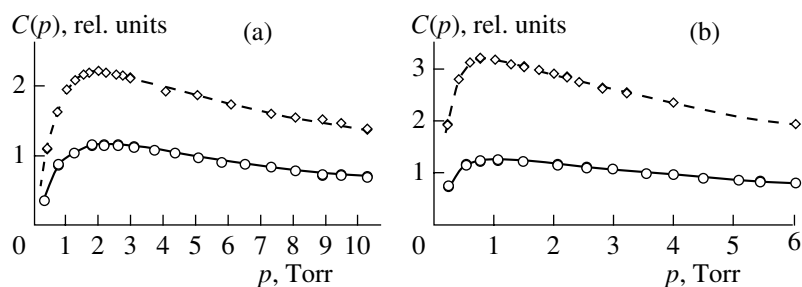


Fig. 4. Dependences of the acoustic cell's sensitivity on the gas pressure for foreign gases: (a) argon and (b) fluoroform. The solid and dotted lines correspond to measurements (dots) in the lines of transitions $J = 1-0$ of CO molecules and $J = 9-8$ of OCS molecules, respectively.

The integral on the right-hand side of expression (5) is the line's integrated absorption coefficient depending only on intensity I_N of the molecular line and the number of absorbing molecules, i.e., on partial pressure p_{abs} of the absorbing gas (the absorbing gas may be in a mixture with another gas that does not absorb radiation within the same frequency range). The integral on the left-hand side of expression (5) can be calculated in relative units of the spectrometer's output signal using an experimental record of the absorption line. Let us denote this integral as $I_{\text{exp}}(p)$ because its value is a function of the pressure. With allowance for the above, the cell's sensitivity function $C(p)$ can be expressed from Eq. (5) as

$$C(p) = \frac{I_{\text{exp}}(p)kT}{P_0 L p_{\text{abs}} I_N}, \quad (6)$$

where T is the temperature and k is the Boltzmann constant.

Formula (6) includes the experimentally measured values of the integrated absorption in the observed line and the partial pressure of the absorbing gas in the cell. The other quantities on the right-hand side of this formula can be considered constant in each particular experiment. This means that the pressure dependence of the cell's sensitivity normalized by a constant factor can be determined experimentally. Two rotational spectral lines—the $J = 1-0$ line of carbon dioxide (CO) at 115271.202 MHz and $J = 9-8$ line of carbonyl sulfide (OCS) at a frequency of 109463.069 MHz—were used for determining the cell's sensitivity function. A mixture of the absorbing gas and a foreign gas in a proportion of $\sim 1 : 10$ was admitted to the cell. Argon and fluoroform were used as foreign gases.

The absorbing-gas line profile was recorded at different pressures in the mixture. Because the percentage of the components in the mixture remained constant during the experiment, the pressure of the absorbing gas was proportional to the total pressure in the mix-

ture, thereby allowing the cell's sensitivity function normalized by an arbitrary factor to be defined as

$$C(p) = \frac{I_{\text{exp}}(p)}{p}.$$

The results of the experiments are presented in Fig. 4. Note that the form of the function $C(p)$ must not depend on which absorption line is used in measurements, because, at the aforementioned ratio of the absorbing and foreign gases in the mixture, the acoustic properties of the mixture are almost entirely specified by the foreign gas. It is of importance that the functions measured for different foreign gases have different characteristic scales (Fig. 4, the upper and lower curves).

Comparison of the results of the cell's sensitivity measurements for the same foreign gas with the use of various absorption lines has shown that the ratio of the thus measured pressure dependences of the sensitivity remain constant within several percent (see Fig. 5). It follows from Eq. (6) that the BWO radiation-power instability is the most probable source of measurement errors of the sensitivity function. This inference is confirmed by additional experiments.

The above example demonstrates the possibility of measuring the acoustic cell's sensitivity function for any gas, thereby allowing studying the absorption in the gas as a function of the pressure, and determines the range of the accuracy of such measurements. If necessary, the cell's sensitivity function can be calibrated in the units of the absorption coefficient with the use of a record of the spectral line with the known (calculated or determined experimentally with a spectrometer of other type) absorption coefficient. Note that the immobility of the setup's waveguide elements during the entire run of experiments is a condition for the applicability of the measured dependence.

4. STUDYING THE ABSORPTION PROFILE

As an example of the abilities of the RAD spectrometer, we present a study of the molecular-absorption

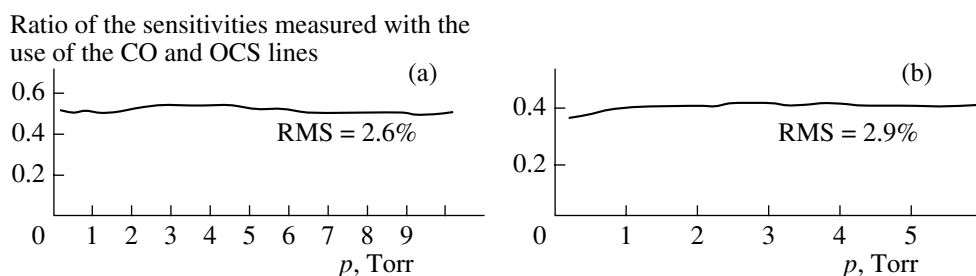


Fig. 5. Ratio of the dependences of the acoustic cell's sensitivity on the gas pressure obtained with the use of lines of CO and OCS gases for foreign gases: (a) argon and (b) fluoroform. RMS is the root-mean-square deviation.

profile for the $J = 9$ rotational multiplet of fluoroform (CHF_3) at pressures of 0.012–6.970 Torr. Fluoroform is a quite rigid and highly oblate symmetric-top molecule characterized by a substantial constant dipole moment. Therefore, in addition to the collisional broadening of lines, the effects of pressure-induced shifts and interference of lines must manifest themselves in the molecular spectrum. This conclusion is confirmed by our previous results [10].

The rotational multiplet of fluoroform is a set of closely positioned lines corresponding to the rotation of the molecule with different projections of the total rotational momentum on the axis of symmetry that are called K components. The number of K components depends on rotational quantum number J and is equal to $J + 1$. At pressures < 0.1 Torr, the components with $K > 3$ are resolved well in an experimental record of the multiplet, but at pressures higher than 0.2 Torr, all lines of the multiplet merge into a combined absorption profile. In this case, an effect of interference of the multiplet's K components can be observed, when the resulting absorption profile is narrower and more intense than the profile formed as the sum of the profiles of separate multiplet's components. In this case, the broadening coefficient of the multiplet as a whole must be appreciably lower than the average broadening coefficient of the K components. In the first approximation (which is linear with respect to the pressure), the manifestation of the effect of interference of lines on the absorption-line profile can be characterized by a single parameter for each of the interfering lines [11]. To determine the parameters of the spectral lines corresponding to the multiplet's components, we used a series of records at fluoroform pressures of 12–79 mTorr. An example of such a record at a pressure of 51 mTorr is shown in Fig. 6. The model function for processing records at each pressure was chosen in the form

$$S_{\text{lp}}(p, \nu) = (A_0 + A_1 \nu) \sum_{K=0}^9 V_K(p, \nu) + A_3, \quad (7)$$

where index "lp" means low pressure, $V_K(p, \nu)$ is the Voigt profile, and A_n are variable parameters allowing for above-mentioned features of the RAD spectrometer.

In addition, such parameters as the collisional widths and the intensities of all lines of the multiplet and their center frequencies, except for unresolved components $K = 0$ and 1, the frequencies of which were assumed to be equal to their calculated values [12] and the intensities were considered identical, were likewise varied during processing of the spectral records.

In this case, the use of the approximation $\alpha L \ll 1$ is justified by the result of auxiliary measurements of the absorption coefficient of this fluoroform's multiplet at the frequency of component $K = 0$. These measurements performed with a videospectrometer having a 1-m-long absorbing gas cell have shown that, at a pressure of 0.4 Torr, the absorption coefficient is $0.0017(1) \text{ cm}^{-1}$. The systematic measurement error ($\sim 0.4\%$) of the line broadening that arises due to the use of the approximation $\alpha L \ll 1$ has been determined via the mathematical simulation method (Fig. 3). An example of the residue of the regression of function (7) to the experimental record in Fig. 6 is shown in the bottom part of Fig. 6 at an enlarged scale. The observed deviations amount to $< 1\%$ relative to the line amplitudes and are virtually of noise origin, thereby indicating the adequacy of model (7).

Figure 7 shows the pressure dependences of the Lorentz widths of the K components for $K = 5, 7,$ and 9 . Dots denote the values resulting from the processing of the experimental records at different pressure values. The statistical errors in determining the linewidths are comparable with the size of the dots in the plot. Straight lines show the results of linear regressions of the obtained dependences. The coefficient of the collisional broadening is numerically equal to the slope of the pressure dependence of the Lorentz linewidth.

Figure 8 shows the experimental results of determining the broadening coefficients for the K components at three different values of the radiation power directed into the cell. Because the components with small K are not resolved even at low pressures, the values of the broadening parameters for these components are determined inaccurately. Nevertheless, with allowance for the fact that the broadening parameter for a K component must be a smooth function of quantum number K , this dependence (the dotted line in Fig. 8) can be plotted with the use of the broadening param-

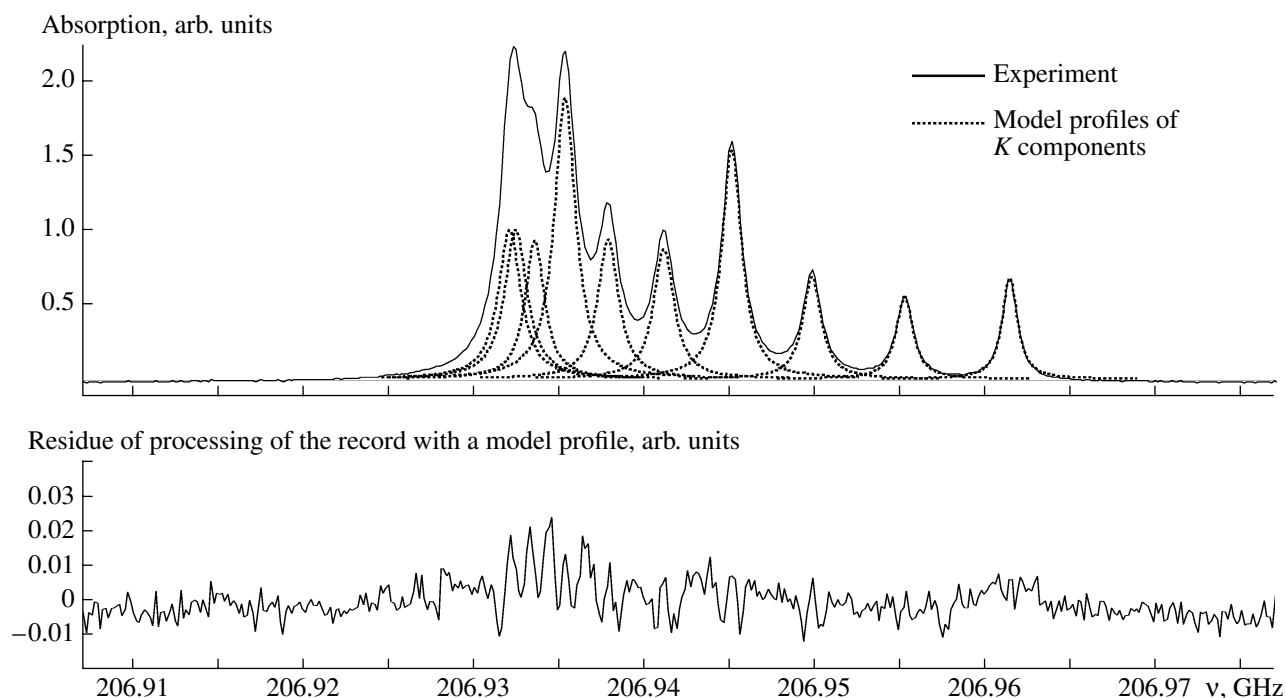


Fig. 6. (Upper curves) Record of the (solid line) absorption profile for fluoroform's multiplet $J = 9$ at a pressure of 51 mTorr and (dotted line) model profiles of the K components composing the multiplet; (bottom curve) residue of the regression of the model function to the experimental record of the absorption profile.

ters resulting from the processing of the experimental data.

The BWO radiation power affects both the broadening parameters and the zero widths (the Lorentz linewidth at a zero pressure obtained via extrapolation) of the K components (Fig. 9). At the lowest power used in experiments, the zero widths of the K components are approximately the same. The widths of a K component at pressure p can be written as $\Delta\nu_K = \Delta\nu_0 + p\gamma_K$, where $\Delta\nu_0$ is the zero width and γ_K is the broadening parameter

of the K component. Quantity $\Delta\nu_0$ allows for both the power-induced broadening and the broadening due to collisions with the cell's walls. Calculations performed in accordance with [6] show that the contribution to the fluoroform linewidth due to collisions with the walls is 2.58 kHz, a value that is small even in comparison to the Doppler broadening, which amounts to 153 kHz under our experimental conditions.

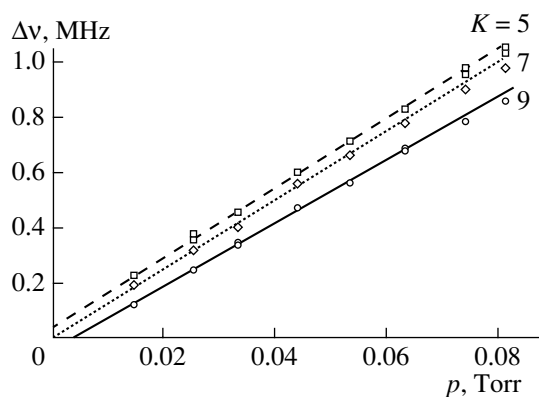


Fig. 7. Experimentally measured (dots) Lorentz linewidths of the $K = 5, 7$ and 9 components of fluoroform's $J = 9$ multiplet at different pressures and (straight lines) the results of their linear regression.

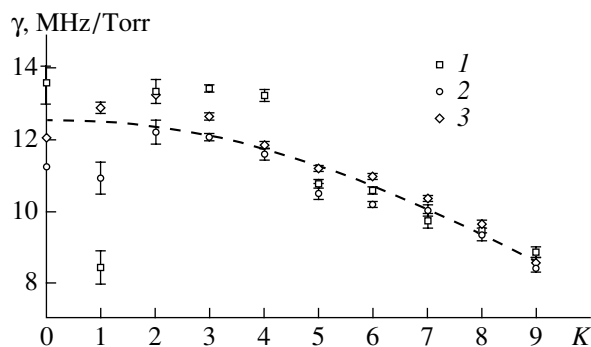


Fig. 8. Results of determining the parameters of the collisional broadening of the lines of K components at different power values: (1) maximum BWO power (~ 20 mW) used during spectrum recording, (2) fourfold power attenuation, and (3) tenfold power attenuation. The dotted line shows the dependence of the broadening coefficient on quantum number K used for plotting the model absorption profile.

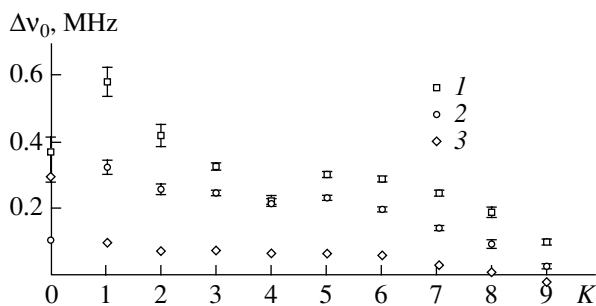


Fig. 9. Zero widths of the K components (obtained as a result of extrapolation to the zero pressure of linear regressions of the Lorentz widths of the corresponding components measured at different pressures) at radiation powers of (1) 20, (2) 5, and (3) 2 mW.

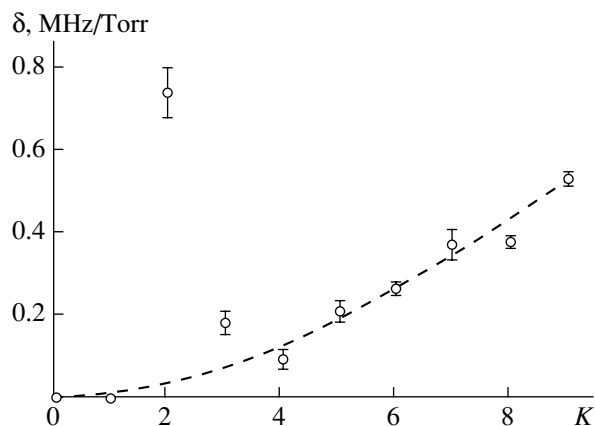


Fig. 11. Coefficients of linear (with respect to the pressure) shift of the center frequencies of the components of multiplet $J = 9$ as a function of quantum number K . Dots are experimental values and the dotted line is the dependence used for plotting the model absorption profile for fluoroform.

Figure 10 shows the pressure dependences of the difference between the center frequencies of the K -component lines observed experimentally and calculated from the constants taken from [12]. The coefficients of the pressure-induced frequency shift that are numerically equal to the slope of this dependence increase smoothly with an increase in K (Fig. 11). The values of the pressure-unshifted center frequencies (Fig. 12) determined from the extrapolation of experimental dependences are on average 10 kHz lower than the calculated ones. This value is beyond the range of errors of the calculated frequencies that are associated with uncertainties in the constants from [12], the values of which are used in the calculations. This slight discrepancy may be due to the fact that the pressure-

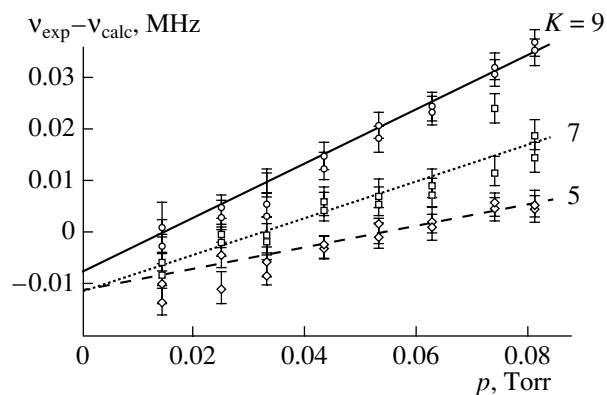


Fig. 10. Deviations of the measured frequency of the line center from the values calculated using the constants taken from [12] for the components at $K = 5, 7$, and 9 (dots) at different pressures and (straight lines) the results of their linear regression.

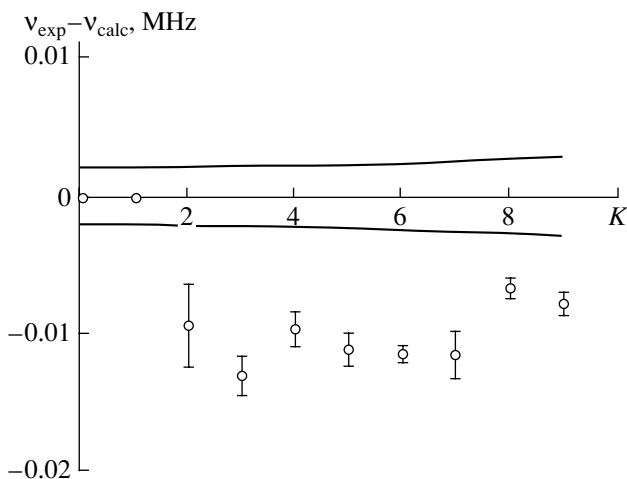


Fig. 12. Difference of the values of pressure-unshifted center frequencies of the K components of multiplet $J = 9$ determined from experimental data and calculated using the constants taken from [12]. Solid lines show the limiting errors of the calculated frequencies.

induced shift of the line frequencies was not considered in [12].

To study the possible manifestation of the interference effect between the components of fluoroform's multiplet $J = 9$, the absorption profiles of the multiplet were recorded at pressures in the range 0.99–6.97 Torr. Examples of such profiles are shown in Fig. 13. At such pressures, the width of each component of the multiplet far exceeds the distance between the extreme components. Therefore, the total absorption profile of the multiplet can be approximated quite accurately by a Lorentz profile, as was performed, e.g., in [10]. This profile corresponds to an isolated line broadened by collisions with a center frequency corresponding to the

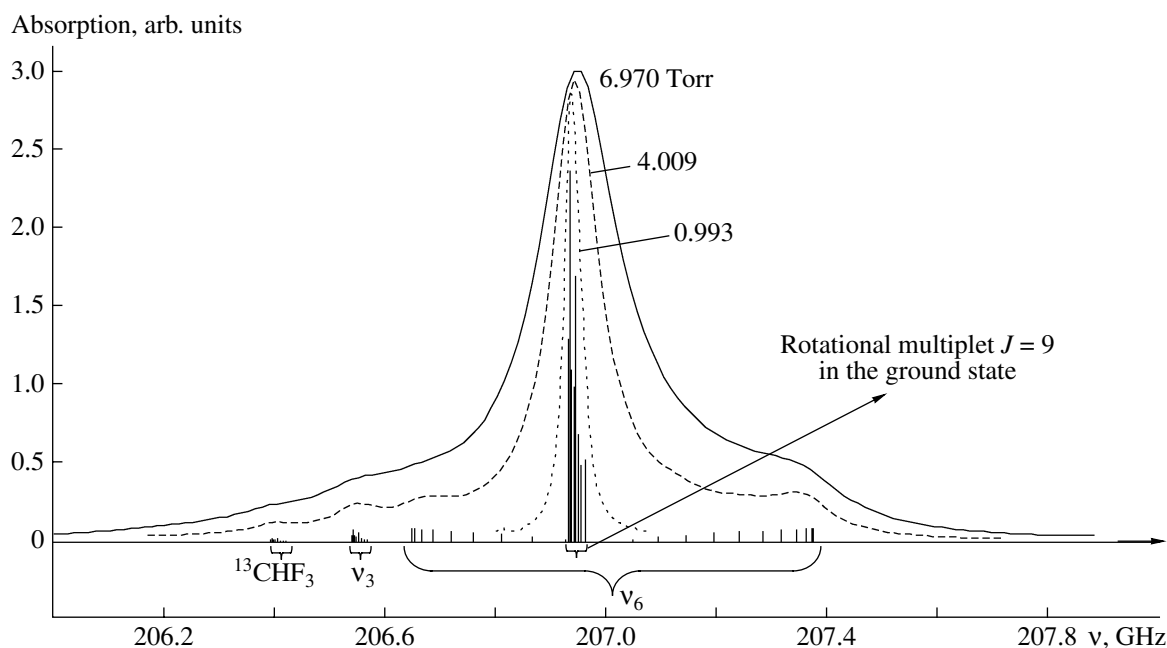


Fig. 13. Examples of records of the absorption profile for fluoromethane's multiplet $J = 9$ at high pressures (indicated by figures near curves). Vertical lines denote the positions of the components of multiplet $J = 9$ of isotopolog $^{12}\text{C}\text{CHF}_3$ in the ground vibrational state, the components of multiplet $J = 9$ of isotopolog $^{13}\text{C}\text{CHF}_3$ in the ground vibrational state, and the lines corresponding to the transitions of the main isotopolog in the excited ν_3 and ν_6 vibrational states, which are considered during simulation of the fluoromethane absorption profile.

weighted mean (with allowance for the amplitudes of the components) frequency of the multiplet. This means that the records shown in Fig. 13 in the central part of the multiplet, i.e., in the frequency range corresponding to the records at a low pressure, can be processed with the use of the following model function:

$$S_{\text{cent}}(\nu) = \text{Lor}(\nu)(A_0 + A_1\nu) + A_2 + A_3\nu, \quad (8)$$

where $\text{Lor}(\nu)$ is the Lorentz profile.

The use of function (8) made it possible to find the pressure dependence of the width of the merged multiplet and, from the linear regression of the obtained dependence, to determine the broadening parameter. The latter value equal to 11.49(4) MHz/Torr coincides, within the experimental error, with the average value (11.78(40) MHz/Torr) of the broadening coefficients of individual K components of the multiplet measured at a low pressure.

This coincidence allows an assumption that interference does not manifest itself between the multiplet's K components. The coincidence of the observed absorption profile with the model profile, which results from the summation of the absorption profiles for separate components of the multiplet, would be a confirmation of this assumption.

In addition to the aforementioned K components of multiplet $J = 9$, which correspond to the fluoromethane's ground vibrational state and the parameters of which were determined from an experiment at low pressures, the model profile must include the contribution of weak

lines. These lines correspond to the components of the transition at $J = 9$ in the ν_3 and ν_6 vibrational states and to the ground vibrational state of the isotopic configuration of fluoromethane with a ^{13}C atom, and fall within the spectral range recorded at high pressures.

The positions and relative amplitudes of the lines considered in the model profile are marked with vertical lines in Fig. 13. When absorption was simulated, it was assumed that all considered lines have Lorentz profiles. The frequencies and relative amplitudes of the multiplet's components in the ν_6 degenerate vibrational state were calculated from the spectroscopic constants from [13]. The frequencies of lines in the ν_3 state and for the isotopolog with ^{13}C were calculated using the constants from [11]. The relative amplitudes of the multiplet's components in the ground and in the ν_3 non-degenerate vibrational state were calculated from the known molecular constants and relationships for symmetric-top molecules [6]. To consider the population of the ν_3 and ν_6 states at room temperature, the vibrational frequencies [14] and Boltzmann distribution were used. The amplitudes of the $^{13}\text{C}\text{CHF}_3$ lines were normalized to the natural abundance of the ^{13}C isotope. The center frequencies, the parameters of the frequency shift, and the parameters of the pressure-induced broadening of the multiplet's components in the ground vibrational state were extracted from the aforementioned experimental results at a low pressure. The experimentally measured values of the broadening parameters of the ground

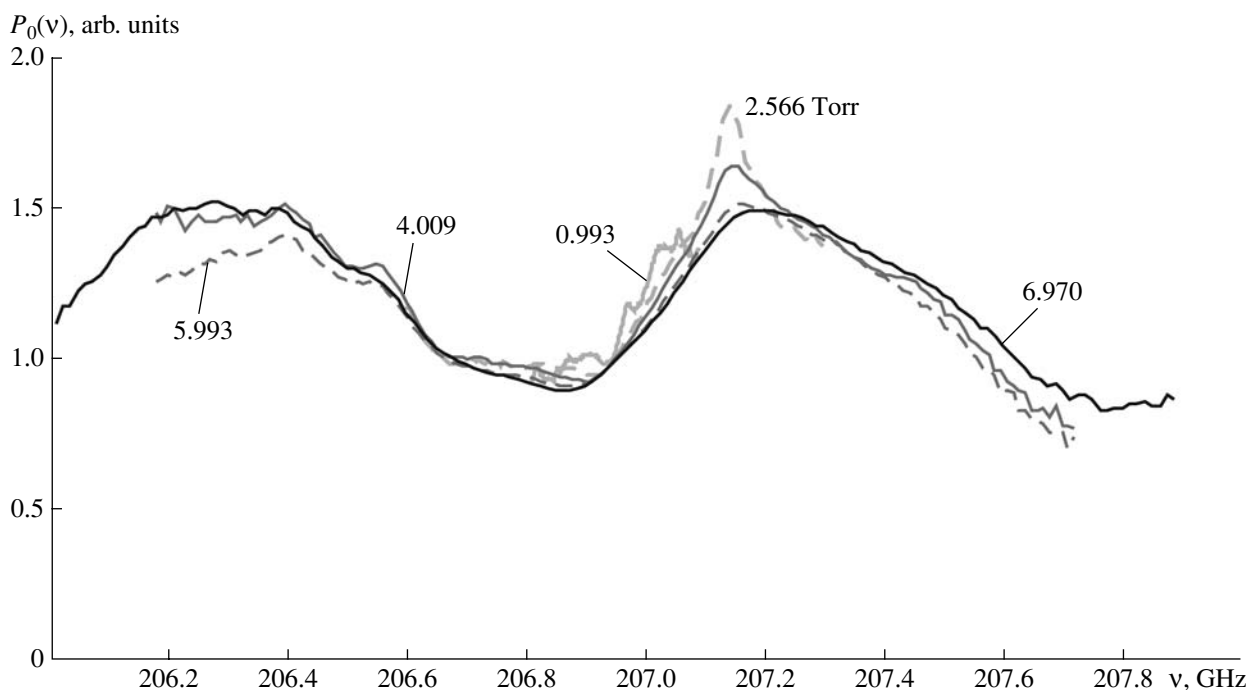


Fig. 14. Experimentally determined frequency dependences of the radiation power $P_0(\nu)$ at the input of the spectrometer's cell extracted from the records of the absorption profiles at different pressures of fluoroform (indicated by figures near curves).

vibrational state lines were also used for the lines in the ν_3 and ν_6 states and for the $^{13}\text{CHF}_3$ lines with corresponding quantum numbers K . This assumption is justified by the well-known fact of the insignificant vibrational and isotopic dependence of the broadening relative to the dominant contribution of the rotational motion of molecules to the broadening.

Apart from thus obtained gas absorption coefficient (α_{CHF_3}), the model profile corresponding to expression (3) must take into account the frequency dependence of the power radiation, the cell's sensitivity as a function of the pressure, and the instrument signal. To reveal the instrument signal, a spectrum was recorded under the same experimental conditions for the argon-filled cell of the spectrometer at a pressure of 2 Torr (argon does not absorb radiation within this frequency range). This spectrum has shown that no instrument signal exceeding the experimental noise within this frequency range is present at the used power level of the radiation source, i.e., $\beta = 0$. The function of the RAD cell's sensitivity for fluoroform was determined experimentally (see Section 3).

Hence, the model profile for this experiment at a high pressure is written in the form

$$S_{\text{hp}}(\nu, p) = P_0(\nu)C(p)\alpha_{\text{CHF}_3}(\nu, p). \quad (9)$$

Note that the frequency dependence of the radiation power is determined not only by the BWO characteristics, which more likely specify certain average power level \bar{P}_0 , but also, to a much higher degree, by the radi-

ation interference pattern, which forms due to multiple reflections of radiation from the cell's windows and other elements of the spectrometer's waveguide channel. Hence, the average radiation power must be a periodic function of the frequency, and the characteristic period of the dependence must be of an order of $c/2l$, where c is the velocity of light and l is the maximum of the characteristic distances between the reflecting elements of the channel. At a 13-cm size of the cell used in our experiments, the characteristic frequency of the dependence is expected to be 1.15 GHz. This estimate shows that the use of a power function for approximating $P_0(\nu)$ in a frequency range of ~ 1.8 GHz, which corresponds the considered experiment, is irrelevant. Nevertheless, a natural assumption is that, at a stationary mutual arrangement of the elements in the spectrometer's waveguide channel, the function $P_0(\nu)$ must not depend on the gas pressure in the cell (to within a slight change in the refractive index). This circumstance means that, under the assumption of the validity of formula (9), which is written without allowance for the interference of the multiplet's components, the dependences $P_0(\nu)$, determined on the basis of (i) the experimental spectra $S_{\text{hp}}^{\text{exp}}(\nu, p)$ recorded at various pressures; (ii) the known sensitivity function $C(p)$; and (iii) the available data for calculating $\alpha_{\text{CHF}_3}(\nu, p)$ as

$$P_0(\nu) = \frac{S_{\text{hp}}^{\text{exp}}(\nu, p)}{C(p)\alpha_{\text{CHF}_3}(\nu, p)}$$

must coincide within the experimental error.

The result of this processing is presented in Fig. 14. As is seen, the dependences $P_0(\nu)$ at different pressures coincide to within an accuracy of several spikes (which may be due to the presence of weak impurity lines disregarded during simulation of the gas absorption coefficient), thereby confirming the validity of the suggestion of the absence of interference effects between the multiplet's K components in the given pressure range.

5. CONCLUSIONS

The factors affecting the accuracy of determining the parameters of molecular lines in the RAD spectrometer, including the instrumental features of the RAD spectrometer that were not studied earlier, have been considered: the dependence of the sensitivity of the radioacoustic cell on the pressure of the cell-filling gas and the allowance for the frequency dependence of the radiation power in the cell at gas pressures below 10 Torr. A technique for measuring the pressure dependence of the radioacoustic cell's sensitivity is presented. It has been shown that the pressure dependences of the cell's sensitivity are different for different gases and confirmed that the shape of the pressure dependence of the sensitivity does not depend on the choice of the absorbing gas used in the experiment (provided that its concentration is much lower than that of the foreign gas).

With allowance for the considered features of the spectrometer, we have studied the parameters of the lines of fluoroform's rotational multiplet $J = 9$ at a gas pressure changing by almost three orders of magnitude—from 0.015 to 7 Torr. It has been shown experimentally that the K components of purely rotational multiplets of fluoroform exhibit no indications of interference even at a pressure at which all components merge into a single collision-broadened line.

Hence, this study has shown that detailed knowledge of the specific feature of the RAD spectrometer not only allows minimization of the systematic errors during measurements of the parameters of spectral lines but also enhances the capabilities of the experiment, in particular, allowing studies of the pressure dependence of the absorption coefficient.

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