============ **SPECTROSCOPY OF ATOMS** ============
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Low Rotational Transitions of the CF$_3$H Molecule: The Pressure-Induced Shift and Broadening

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Received April 15, 2005

Abstract—Using a microwave spectrometer with a radioacoustic signal detection, the absorption profiles in the multiplets of the low rotational transitions $J'-J = 2–1$, $3–2$, $4–3$, and $5–4$ of the ^{12}CF$_3$H molecule in the ground vibrational state at pressures of pure gaseous CF$_3$H from 0.1 to 1.3 Torr when all the K components of the multiplets merge into a single spectral line are studied. The parameters of the pressure-induced shift and broadening of the observed lines are determined by comparing the theoretically modeled absorption signal and the experimental spectrum. The model used takes into account weak lines corresponding to the excited vibrational states ν_3 and ν_6 of the ^{13}CHF$_3$ molecule and the instrumental features of the spectrometer. The observed multiplet is simulated as an isolated Lorentzian line and as a sum of the profiles of the K components with known unshifted positions and known amplitude ratio. The shift and broadening parameters obtained in both cases are shown to agree well with each other. The dependences of the shift and broadening parameters on the quantum number J are analyzed and compared with the previously obtained data for the lines $J'-J = 1–0$ and $2–1$.

PACS numbers: 33.20.V

DOI: 10.1134/S0030400X06050080

INTRODUCTION

The CF$_3$H molecule (fluoroform or trifluoromethane), being one of the trace gases in the Earth's atmosphere, has also been discovered recently in the Martian atmosphere [1]. The investigation of the CF$_3$H spectrum is interesting from both basic and applied points of view. The applied interest is due not only to atmospheric problems, but also, to a large extent, to the use of fluoroform as a working gas in many industrial processes, such as plasma etching in the production of semiconductor microassemblies [2], growing artificial diamonds [3], and fabrication of thin films with preset properties [4]. Monitoring of such industrial processes is carried out, in particular, by the methods of microwave spectroscopy in both the millimeter [5] and the submillimeter wavelength regions [6]. The basic interest in fluoroform is connected with the fact that various and relatively poorly studied collisional effects (pressure-induced shift and broadening of lines, interference of lines) that determine the absorption profile of individual lines and bands should manifest themselves in the spectrum of this molecule, which is a symmetric top and has a large dipole moment.

The effective spectroscopic constants of the rotational spectrum of the CF$_3$H molecule and its main isotopomers in the ground and two low vibrational states ν_3 and ν_6 are well known [7, 8]. Therefore, the positions of the CF$_3$H spectral lines can be calculated to a high accuracy (several kilohertz for the main isotopomer in the ground vibrational state). At the same time, information about the pressure-induced broadening of the CF$_3$H spectral lines is severely limited. As far as we know, only one paper [9] presents experimental and calculated data on the line broadening parameters for the two lowest rotational transitions $J–J' = 1–0$ and $2–1$ of the main isotopomer of the CF$_3$H molecule in the ground vibrational state.

The aim of this work is to study the pressure-induced broadening and shift of spectral lines of the CF$_3$H molecule corresponding to the low rotational transitions $J'-J = 2–1$, $3–2$, $4–3$, and $5–4$ in pure gas. Each transition is a multiplet, consisting of $J + 1$ components, which correspond to the different projections of the total angular momentum **J** onto the molecular axis, characterized by the quantum number K. Since the molecule is quite rigid, the split of the low transitions into K components is rather small, and, at a gas pressure higher than ~0.1 Torr, all the multiplet components merge to form a single collisionally broadened spectral line. The parameters of such lines are the objects of investigation in this work.

EXPERIMENT AND DATA PROCESSING

For the investigation, we used a microwave spectrometer with a radiation frequency synthesizer based on backward-wave oscillator (BWO) tubes, stabilized by a phase lock-in loop (PLL) system by the harmonic of a high-stability radio signal, and the radioacoustic detection of the absorption signal, which was reported
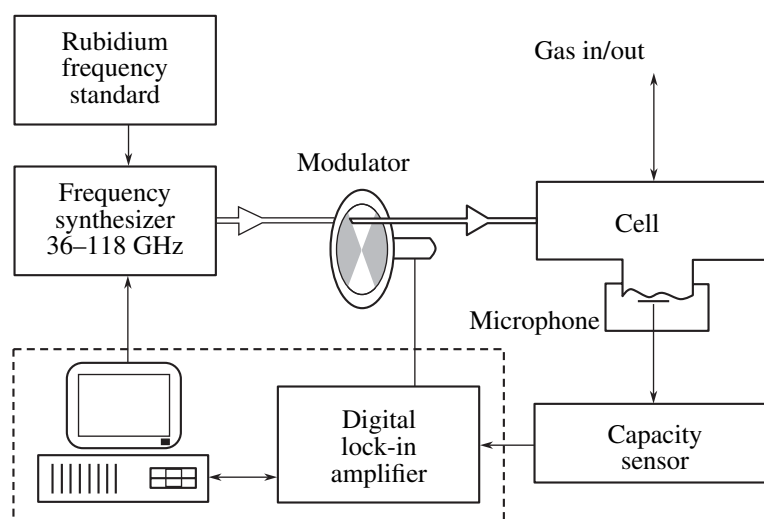
Fig. 1. Simplified schematic diagram of a spectrometer with a frequency synthesizer and radioacoustic detection of the absorption signal.

in [10]. A simplified schematic diagram of the spectrometer is shown in Fig. 1. In all the experiments, the radiation sources were synchronized by using a 5-MHz reference signal of an SChV-74 rubidium frequency and time standard. The full width at half maximum of the spectrum of the radiation source of the spectrometer was on the order of several kilohertz, while the relative stability and frequency adjustment accuracy of the radiation amounted to ~10^{-9} at an output radiation power of about 10 mW.

The synthesizer frequency was scanned with a preset step, and the absorption signal was recorded with the aid of a computer. The frequency step was varied depending on the gas pressure in a cell and was chosen so that the width of the spectral interval containing a line under study corresponded to 8–10 half-widths of this line and could be recorded in ~150 steps. We used 100% amplitude modulation of the radiation with a frequency of 180 Hz and synchronous detection of the absorption signal at the modulation frequency.

In the experiments, we used a gas cell whose cylindrical absorbing part was 100 mm in length and 16 mm in diameter. A vacuum system for filling and pumping of the gas cell contained a ballast volume for the pressure stabilization in the system during the experiment. This volume exceeded the cell volume roughly tenfold. The gas pressure in the system was controlled by a baratron (MKS, model 627BX11TDC1B, pressure range of 0.001–10 Torr). The system was evacuated by a mechanical backing pump down to a pressure of ~10^{-3} Torr and then by a cryogenic zeolite pump down to 10^{-4}–10^{-5} Torr. The lower pressure was used for the zero adjustment of the baratron. The accuracy of the gas pressure measurement amounted to ~0.5 mTorr. Gaseous fluoroform for the experiments was supplied by the Irkutsk Institute of Chemistry, Russian Academy of

Sciences. The investigations were carried out at room temperature, which was monitored by a laboratory mercury thermometer with a scale grade of 0.2°C. At the beginning of the experiment, the vacuum system and the gas cell were filled with fluoroform at a pressure of 1.1–1.2 Torr, and then the gas was gradually evacuated down to a pressure ~0.1 Torr.

At each gas pressure, the shape of the line of interest was analyzed by the method of mathematical fitting of a model function of the observed spectrum to the experimental profile. The model function was a sum of the absorption profiles of the multiplet under study and weak lines corresponding to transitions of fluoroform in excited vibrational states, as well as to the ^{13}C isotopomer of fluoroform, whose frequencies fall within the recorded spectral range. In addition, the function included the common multiplicative term linear in frequency that takes into account the frequency dependence of the power of the radiation source of the spectrometer and the common additive term quadratic in frequency that takes into account a weak acoustic signal, arising owing to a nonresonance absorption of the amplitude-modulated radiation power in the cell elements that induces the secondary heating of the gas in the cell. The line profile was taken to be Lorentzian, characterizing the shape of spectral lines in a pressure range in which the collisional broadening prevails. This condition corresponded to the conditions of our experiments. Even at the lowest pressures used in the experiments, the collisional broadening of the CF_3H lines exceeded the Doppler broadening, ranging from 31 to 77 kHz (the half width at half maximum) for various transitions, by more than an order of magnitude. The absorption profile of the studied multiplet was modeled in two ways. At a pressure higher than 0.5 Torr, the half-width of the multiplet profile exceeds severalfold the
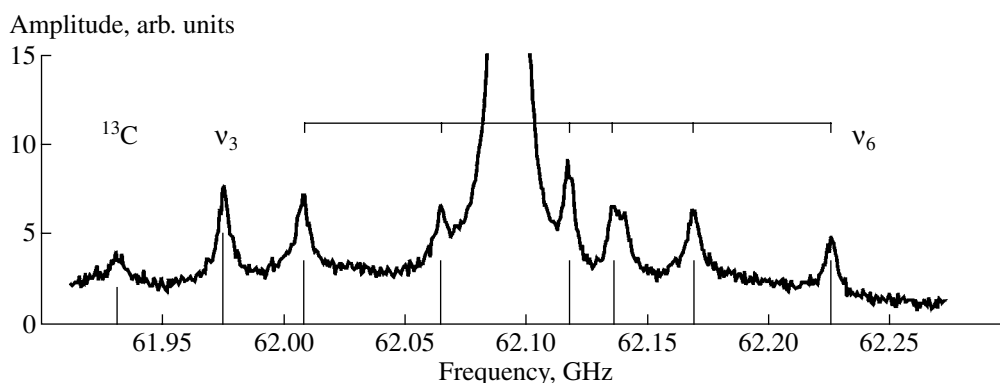
Fig. 2. Record of the CF_3H spectrum near the transition $J = 3\text{--}2$ at a pressure of about 10 mTorr. The strong line at the center of the record, whose maximum is beyond the figure, has an amplitude of ~136 arb. units and belongs to the $^{12}CF_3H$ molecule in the ground vibrational state. The vertical lines show the positions of the known lines, corresponding to the same transition in the other vibrational states (ν_3 and ν_6) and to the isotopomer with the ^{13}C atom.

spacing between its lowest and highest frequency K-components even for the transition $J = 5\text{--}4$. Therefore, in the first model, used mostly to process the records at high pressures, the multiplet profile was represented by a single Lorentzian line. It was assumed that the lines falling within the recorded range have the same width and the ratio of their amplitudes remains constant as the gas pressure varies. The width of the radiation source spectrum is negligibly small as compared to even the Doppler broadening, and therefore its influence on the profile of the observed lines was neglected. Thus, the first model function was written in the following form:

$$ S(f) = \left[M_1(f) + A_0 \sum_n \frac{A_n}{\Delta f_0^2 + (f - f_n)^2} \right] $$
$$ \times (1 + B_1(f - f_0)) + (1 + B_2(f - f_0) + B_3(f - f_0)^2), $$

where $M_1(f) = A_0/[\Delta f_0^2 + (f - f_0)^2]$ is the profile of the multiplet line; f is the current frequency; A_0, Δf_0, and f_0 are variable parameters corresponding to the amplitude, half-width, and central frequency of the line of the studied multiplet; the summation is performed over all weak lines of the excited vibrational states falling near the line of the studied multiplet; f_n and A_n are fixed parameters corresponding to the frequencies and amplitudes of these lines normalized to the amplitude of the multiplet; and B are variable parameters taking into account the spectrometer features.

The second model, used mostly at low pressures, differed from the first one in the following. The line of the multiplet was represented as a sum of the profiles of all the K components with the use of their calculated pressure-unshifted positions f_K and relative amplitudes A_K. It was assumed in this case that all the components have the identical widths Δf_0 and the same pressure-

induced frequency shifts δ. Thus, the profile of the multiplet line in the second model was written in the form

$$ M_2(f) = A_0 \sum_K \frac{A_K}{\Delta f_0^2 + (f - f_K - \delta)^2}. $$

The parameter δ was also varied.

The positions of the weak lines, corresponding to the vibrational states ν_3 and ν_6 and to the isotopomer with ^{13}C, were calculated by using the constants from [11]. The positions of other weak lines were determined from the spectra recorded at low pressures. Such a record of the CF_3H spectrum near the transition $J = 3\text{--}2$ at a gas pressure of about 10 mTorr is exemplified in Fig. 2. The strong line at the center of the record belongs to the multiplet of the main isotopomer of fluoroform in the ground vibrational state. Its amplitude is ~136 arb. units. To determine the amplitude ratio of the weak lines to the multiplet line, we used the calculated and experimental data. This ratio was ~3% for the most intense of the observed weak lines for all the studied transitions.

The records of the fluoroform spectrum in the vicinity of the transition $J = 4\text{--}3$ at different pressures, used to determine the collisional parameters of the line corresponding to this transition, are exemplified in Fig. 3. The vertical lines in the figure show the positions and scaled-up relative amplitudes of the weak lines taken into account in the processing. The residuals of the processing of some of the records shown in Fig. 3 with the first model function $S(f)$ are shown in Fig. 4 in the same amplitude units as the lines shown in Fig. 3. The small systematic deviations of the residuals from an even noise level are smaller than 0.3% of the multiplet amplitude, which is also typical for the processing of the records at other pressure values, as well as for multiplets of other transitions, for which such deviations also did not exceed 0.3–0.5%.
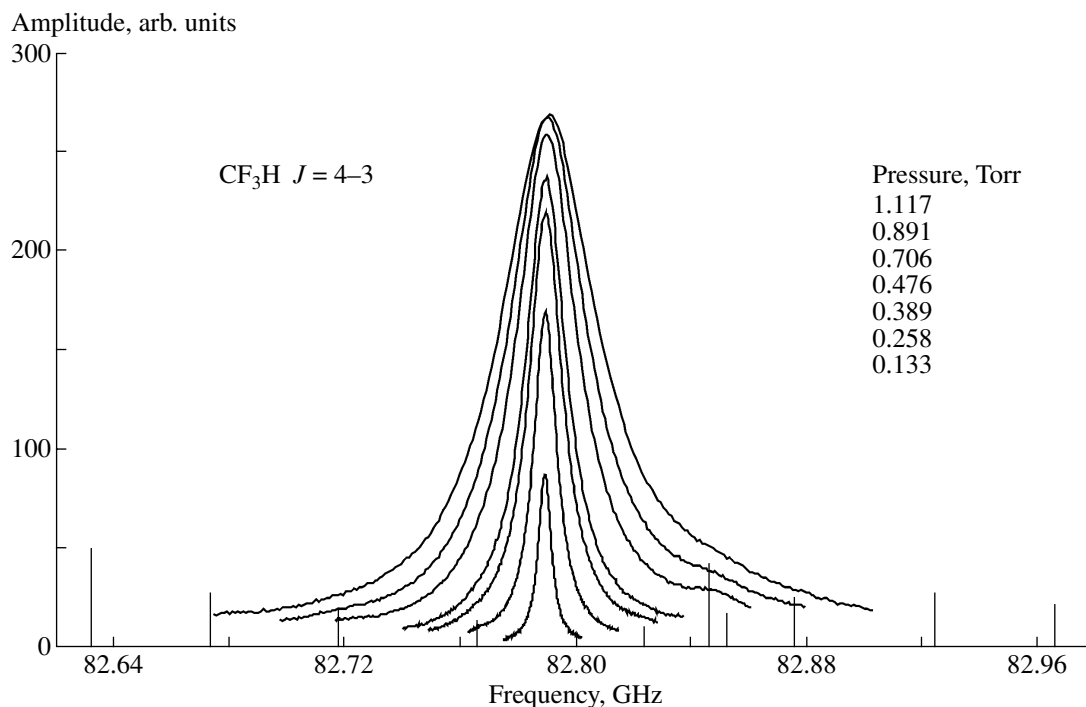
Fig. 3. Record of the multiplet line $J = 4$–3 of CF_3H at different pressures. The line with the maximal amplitude corresponds to the maximal pressure. The pressure values are given in the figure. The vertical lines on the abscissa axis indicate the positions and scaled-up relative amplitudes of the weak lines, taken into account in the processing of the measurement results.
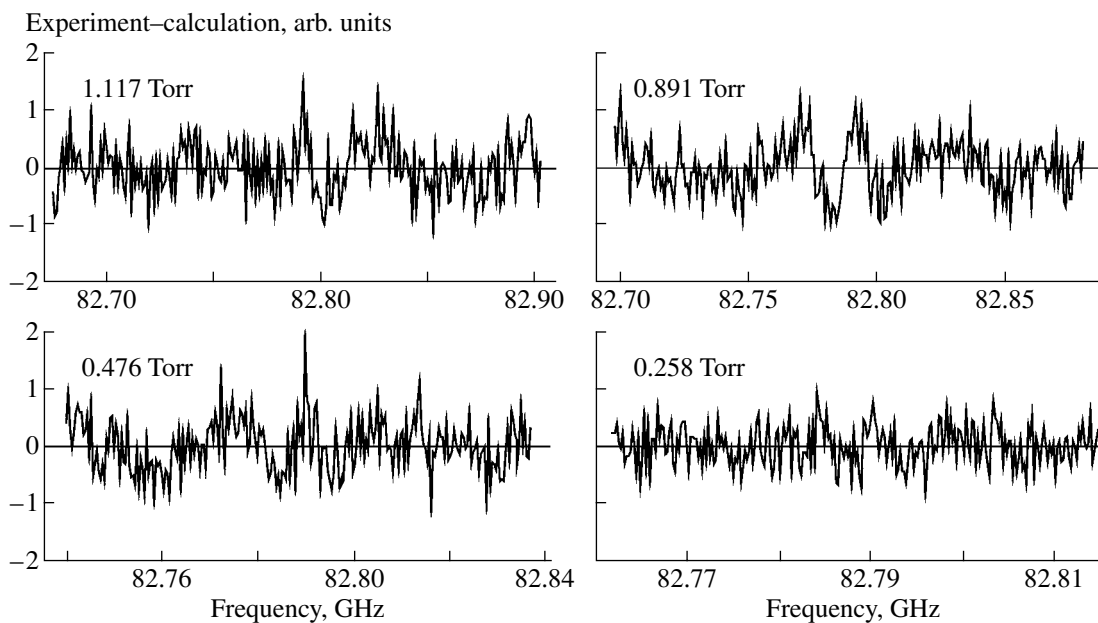

Fig. 4. Examples of the residuals from the processing of the records of the CF_3H line $J = 4$–3 with the first model function $S(f)$ at different pressures. The pressure values are given in the figure.

The obtained values of the width Δf_0 and the central position f_0 at different pressures were then used to determine the parameters of the pressure-induced broadening and shift, whose values were found as a slope of the corresponding linear function, giving the best fit to the experimental values.
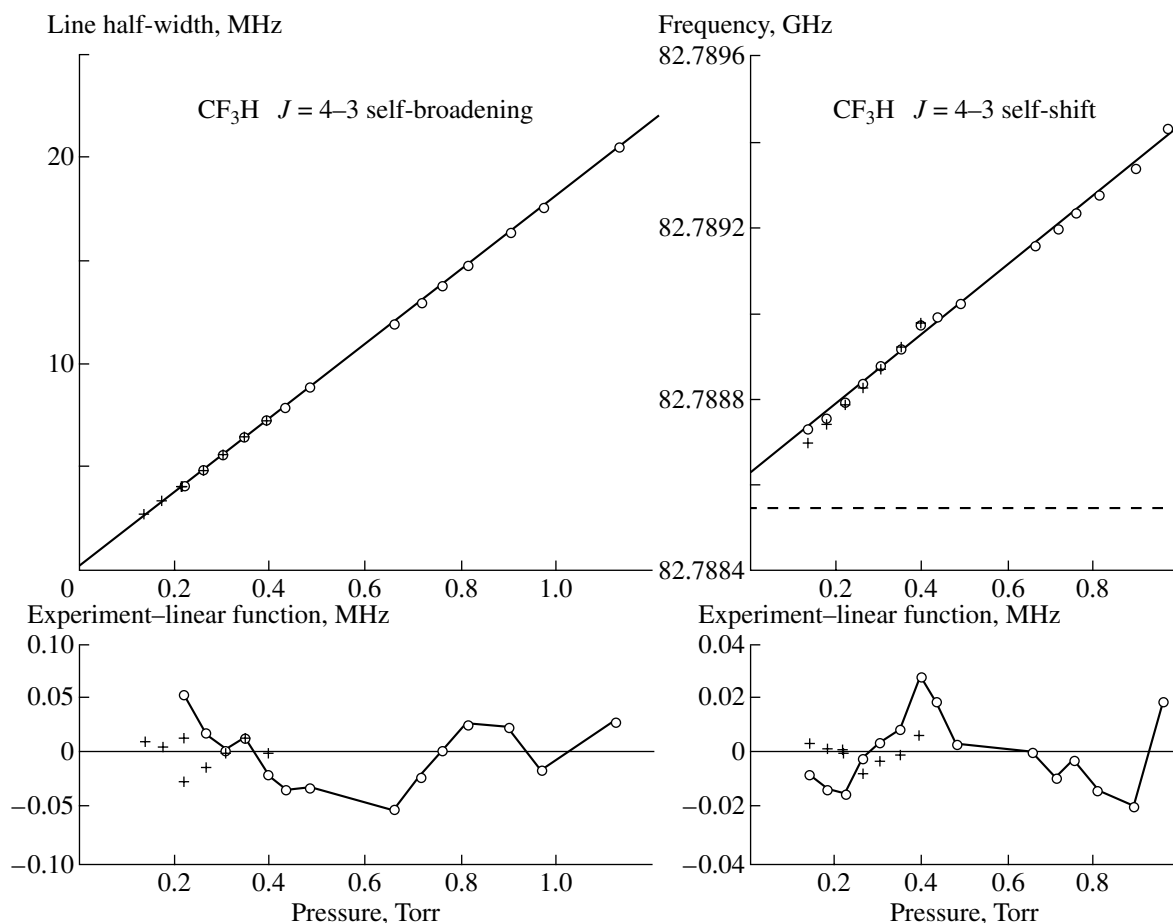
Fig. 5. Pressure dependence of the width (left) and the central position (right) of the CF$_3$H line corresponding to the transition $J = 4$–3. Circles in the plot are the experimental values obtained from the processing of the line records with the first model function $S(f)$, and solid curves correspond to the linear regression of these values. Crosses indicate the values obtained from the processing of the records with the second model function. The bottom part of the figure shows the differences between the experimental values and the corresponding linear functions. The average weighted frequency of the transition is shown by the dashed line in the top right plot.

The top part of Fig. 5 shows the pressure dependences of the width (left) and the central position (right) of the line corresponding to the transition $J = 4$–3. The circles on the plot stand for the experimental values obtained from the processing of the records with the first model function and the solid lines are the linear regressions of these values. The bottom part of the figure depicts the differences between the experimental values and the linear function, demonstrating a rather good linearity of the dependences obtained. Nevertheless, it can be seen that the values of the line width at low pressures lie systematically above the linear dependence. This is connected with the manifestation of the line splitting into the K components, which is ignored in the first model. The separation between the lowest and highest frequency components of this transition is about 1.3 MHz, which is only several times smaller than the half-width of the observed multiplet line at low pressures. The second model, which takes into account the K components of the multiplet, was applied to pro-

cess the spectrum records in the vicinity of this transition at a gas pressure ranging within 0.133–0.476 Torr. At pressures higher than 0.343 Torr, both models gave nearly identical results.

The results of the processing with the second model are shown by crosses in Fig. 5. The broadening parameters determined by the first method, but without taking into account the three points corresponding to the lowest pressure, and the parameters determined by the second method nearly coincide, amounting to 18.26(3) and 18.18(5) MHz/Torr, respectively. (The value in parentheses is the statistical error of the parameter determination in units of the last decimal digit, corresponding to 1σ.) The extrapolation of the dependence of the line broadening to zero pressure gives the widths 160(32) and 136(15) kHz for the first and second processing methods, respectively.

It is interesting to note that, in the case of processing with the aid of the first model, the extrapolation of the

line position to zero pressure (the top right plot in Fig. 5) gives a value which is only 60(20) kHz greater than the average weighted frequency of the transition (shown by the dashed line in the figure), determined by using the constants from [7] as $\Sigma A_K f_K / \Sigma A_K$, where f_K and A_K are the positions and the amplitudes of the K components. The crosses in the top right plot are the sum of the average weighted frequency of the transition and the frequency shift δ determined from the processing of the spectra with the second model. The extrapolation of this dependence to zero pressure gives a value that exceeds the average weighted frequency of the transition by 8(5) kHz. It can be seen that the position of the line resulting from the processing with the first model at low pressure appears to be somewhat higher than in the case of the processing with the second model. This is likely connected with the manifestation of the asymmetry of the multiplet line, arising owing to the different amplitude of the multiplet components. The values of the frequency shift parameter were found to be 0.90(3) and 1.08(2) MHz/Torr in the first and the second case, respectively. The difference between the parameters somewhat exceeds the statistical errors of the processing, but the parameters coincide within the systematic errors, which, for the shift parameter, were experimentally estimated to be ~0.1 MHz/Torr.

The shape of the spectral records and the pressure dependences of the observed line width and frequency position obtained for the other transitions of fluoroform studied in this work are similar to those shown in Figs. 2–5.

To estimate the influence of the effect of the transition saturation by the radiation power on the width of the observed line and, as a result, on the value of the pressure-induced broadening parameter, we have additionally performed three comparative series of measurements of the transition $J = 4–3$ upon decreasing the power of the source radiation by 0, 3, and 6 dB. The broadening parameters obtained from the processing of these series coincided within the statistical errors. However, especially at the lowest pressures, we noticed some tendency to a decrease in the line width by fractions of a percent as the power was halved.

RESULTS AND DISCUSSION

Accurate measurements of the collisional parameters of the lines corresponding to the low rotational transitions of fluoroform are difficult owing to the presence of a large number of lines corresponding to excited vibrational states, lying near each line under study and overlapping with it even at low pressures, markedly influencing the observed absorption profile. Since the collisional parameters of these lines are unknown, their influence can be taken into account only within the framework of general assumptions. The first general assumption—the constancy of the ratio of the amplitudes of these lines to each other and to the amplitude of the studied line with varying pressure—seems to be indisputable, because we deal with quite low pressures, at which the line intensities should not be perturbed. The second assumption, in which the broadening and/or shift parameters are taken to be the same for all lines, is correct, strictly speaking, only in the first approximation and can be justified by the smallness of the contribution of these lines to the calculated spectrum. Use of the more correct physical model in the form of the sum of independent collisionally broadened profiles with all unknown parameters is impossible because of a significant correlation between the parameters. Therefore, systematic errors associated mostly with the features of the model chosen for the consideration of weak lines can present an additional source of errors in determination of the parameters of the multiplets studied in this work, besides the statistical measurement errors connected with an imperfect setting of the radiation frequency, with an inaccurate measurement of the pressure, or with the influence of instrumental noise.

The parameters of the lines of the low rotational transitions of fluoroform measured in this work are summarized in the table.

The dependence of the broadening parameter on the rotational quantum number J is shown in Fig. 6. The experimental values of the broadening coefficients obtained in this work are shown by circles. Crosses and dots stand, respectively, for the experimental and calculated values of the coefficients obtained in [9]. The solid curve is a quadratic hyperbola passing through the values measured in this work.

It can be seen that, within the experimental error, the dependence of the measured broadening parameters on J is smooth and physically justified. The extrapolation of this dependence to $J = 0$ gives a value of the broadening parameter equal to 43.3 MHz/Torr, which is in good agreement with the value 44.0 MHz/Torr calculated in [9].

The dependence of the shift of the line position on the quantum number appears to be not so smooth, but, nevertheless, the spread of the points from the quadratic hyperbola does not exceed the experimental errors, and the value of the shift parameter, as expected, decreases with increasing J.

The behavior of the intercept of the width dependence, that is, the line width at zero pressure, seems surprising. The "zero width" for an isolated collisionally broadened line should be equal to zero. However, in our case, each line has a K structure, whose width is quite significant, especially for the transitions 4–3 and 5–4 (see the last column of the table). Nevertheless, the zero width for the transition 2–1 almost coincides with the width of the K structure, while, for the other studied transitions, it is smaller than the width of the K structure and nearly coincides with the result obtained with the use of the second model, in which it should be zero. At present, we have no reliable explanation for this fact.

Measured parameters of the lines of the low rotational transitions of CF_3H

Transition J'–J	Broadening,[a] MHz/Torr	Broadening, MHz/Torr	Shift, MHz/Torr	Zero width, MHz	Zero frequency, calculation,[b] MHz	Width of the structure,[c] MHz
1–0	38[d]	–	–	–	–	0
	44.0[e]					
2–1	18[d]	28.7(5)	1.7(3)	0.1(1)	0.04(10)	0.07
	36.1[e]					
3–2	–	21.6(5)	1.1(1)	0.3(1)	0.09(10)	0.44
4–3	–	18.2(5)	0.92(10)	0.2(1)	0.06(10)	1.3
5–4	–	15.5(5)	0.84(10)	0.4(1)	0.04(10)	2.9

Note: [a] Data from [9].
[b] The average weighted frequency of the transition determined by using the constants from [7] is taken as a calculated frequency.
[c] The distance between the highest and lowest components of the K structure.
[d] Experiment.
[e] Calculation.

Supposedly, the decrease of the zero width can be explained by the interference collapse of the rotational structure with increasing gas pressure. However, to clarify this in more detail, it is necessary to study higher J multiplets, in which the line structure can be resolved. We plan to carry out such investigations in the near future.

The positions of the lines at zero pressure coincide with the average weighted frequencies of the transitions within several tens of kilohertz, which is indicative of the good agreement between the experiment and the existing notions.

Thus, in this work, we have measured the coefficients of the pressure-induced line broadening and shift for four multiplets of the low rotational transitions of the CF_3H molecule at pressures at which all the K components of the transitions merge to form a single collisionally broadened line. The accuracy of the parameters found is determined by systematic errors and amounts to several percent for the broadening coefficients and about 10% for the shift coefficients. The dependence of the broadening and shift parameters on the rotational quantum number has a smooth character within the measurement errors. The measured broadening parameter for the transition $J = 2$–1 and the broadening parameter of the transition $J = 1$–0 obtained from the extrapolation of the dependence are in good agreement with the data previously obtained in [9]. The shift parameters of the rotational transitions of CF_3H have been measured for the first time. The data obtained can be used both to check the theoretical models of intermolecular interactions and to monitor the processes in plasma reactors by the methods of microwave spectroscopy.
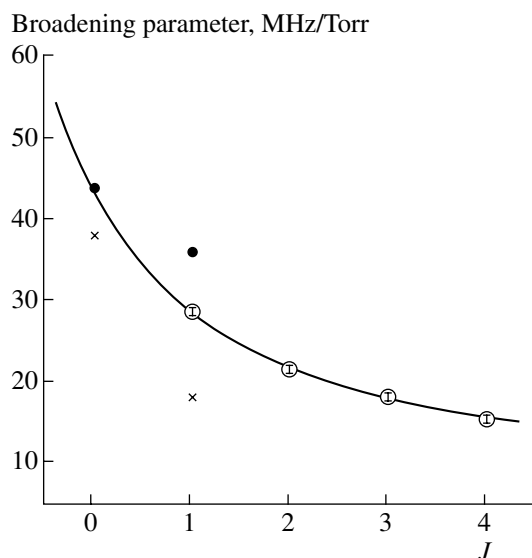

Fig. 6. Dependence of the broadening parameter of the multiplets of the low rotational transitions of the CF_3H molecule on the quantum number J. Circles indicate the experimental values obtained in this work. The measurement errors are shown inside the circles. The solid curve shows the quadratic hyperbola passing through the measured values. Crosses and dots correspond to the experimental and calculated values from [9].

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Translated by A. Malikova