COLLISIONAL COUPLING OF THE MOLECULAR OXYGEN $^{16}O_2$ FINE-STRUCTURE LINES UNDER LOW PRESSURES

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We consider collisional coupling between the fine-structure lines of molecular oxygen near 60 GHz under pressures of up to 20 Torr. The observation possibility of the coupling effect manifestation in the oxygen line profile is analyzed by means of numerical simulation. The signal-to-noise ratio required for direct observation of the collisional coupling and deviations of the line parameters from the tabulated values related to the indirect effect manifestation in the spectra are numerically evaluated. By the example of the overlapping profiles of the 13+ and 3− lines, the impact of collisional coupling on the doublet profile is experimentally demonstrated. The results of the analysis of experimental spectra are in good agreement with the results of numerical simulation.

1. INTRODUCTION

The study of the oxygen absorption band near 60 GHz is important for solving applied problems related to global monitoring of the Earth's atmosphere. Instruments for remote microwave sensing of the atmosphere are located on ground-based stations, aircraft, and satellites. Thermal radiation of the atmosphere in a certain frequency range is measured with the help of radiometers. The basic physical mechanisms that determine the electromagnetic thermal radiation of the atmosphere are the same as the mechanisms that determine the absorption of low-intensity electromagnetic waves by the atmosphere. The main contribution to the absorption is provided by molecular oxygen and water vapor. The solution of modern applied problems requires high-accuracy information on the value of this absorption as a function of the meteorological parameters of the atmosphere. Among such problems, we should mention first of all the study of the Earth's radiation balance, as well as the construction of the atmospheric radiative transfer models (RTM) used for the development of the systems of radio communication, radar, weather prediction, remote sensing of the atmosphere and the Earth's surface, etc. [1].

For a correct interpretation of the atmospheric line profiles recorded with radiometers, we need an absorption model based on the parameters of the profiles of these lines accurately measured in laboratory conditions. The band profile near 60 GHz is significantly affected by the collisional coupling of spectral lines, also called the line interference effect, or spectral exchange [2]. As is shown in [3], this effect has a notable impact on both the absorption coefficient and the refractive index of atmospheric air at frequencies near 60 GHz. Allowance for the collisional coupling effect on the line profiles requires the use of appropriate models containing additional parameters of the line shape. One of the approaches to describing collisional coupling involves the introduction of only one parameter (the so-called first-order collisional coupling parameter) for the profile of each line. Using this parameter, one approximately describes the antisymmetric (relative to the center frequency) linear (in pressure) distortion of the line profile, caused by the collisional coupling

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TABLE 1. Collisional coupling coefficient y of the doublet lines $N = (13+, 3-)$ in atmospheric air ($T = 296$ K) in different papers.

	y, bar^{-1} ([7])	y, bar^{-1} ([8])	y, bar^{-1} ([3])	y, bar^{-1} ([9])	y, bar^{-1} ([10])
$N = 3-$	-0.905	-0.364	-0.216	-0.352	-0.357
$N = 13+$	0.068	-0.384	-0.173	-0.376	-0.311

(a detailed description of this approach is given in, e. g., [3, 4]). To determine the parameter values, the experimental recordings of the oxygen absorption spectra are approximated by model profiles. The accuracy of information about the atmosphere extracted by radiometry is directly dependent on the accuracy of the laboratory data.

Information on the collisional coupling coefficients of the molecular oxygen lines is not given in the most famous spectroscopic databases, such as HITRAN [5] and GEISA [6]. For the fine-structure lines of the O_2 molecule that make up a band near 60 GHz, this is due to the fact that the coefficient values known to date were obtained by solving the ill-posed inverse problem. Namely, band profile records under atmospheric pressure, where all the lines merge into a single contour, were used. As a result, in different models that provide a comparable accuracy of describing the general absorption profile, the coefficient values for each specific transition can differ by several times, and have different signs in some cases [3, 7–10] (see Table 1).

The coefficient values from [7] and [3] are notably different from similar values given in [8–10]. This can be explained by the fact that the authors of [8–10] use the same method for solving the inverse problem to obtain a set of collisional coupling parameters of the fine-structure lines of molecular oxygen constituting a band near 60 GHz. The features of the collisional coupling of the 60-GHz band lines, which were neglected in the calculations in [8-10], were taken into account in [7] when the coefficients were calculated. Paper [3], which was published in 1981, relies on the earlier experimental data on the profile of the band under study and primary parameters of the fine-structure lines (center frequency, intensity, and broadening coefficient). A method for calculation of the collisional coupling parameters, which is based on the semiclassical approach [11] and is different from that used in [7–8], is also employed in [3].

It should be noted that at low pressures, when collisional coupling could be observed for separate or at least resolved lines, the effect is poorly manifested [3]. For this reason, the measurement data on the collisional coupling of individual lines of the fine structure of molecular oxygen are absent for now.

The objective of this paper is to study the influence of the collisional coupling on the shape of the spectral lines that make up the absorption band of an oxygen molecule near 60 GHz. We analyze the possibility of detection of this effect in the profiles of individual lines and closely located pairs of lines (doublets). By the example of the $N = (13+, 3-)$ doublet, the manifestation of collisional coupling under conditions of weak overlapping of the line contours, i. e., at low pressures, is demonstrated and estimates of the collisional coupling parameters for selected lines are given.

The paper consists of several sections, which outline brief information on the spectrum of molecular oxygen in the millimeter wavelength range, the principles of spectrum modeling with allowance for collisional coupling, analysis of the possibility of direct and indirect observation of the collisional coupling effect, the technique of recording the line profiles using a spectrometer with radio acoustic detection of absorption and preliminary processing of the obtained data, the results of analysis of the experimentally recorded line profiles under different conditions and the conclusions drawn from the data obtained.

2. THE 60-GHz OXYGEN ABSORPTION BAND

Consider the structure of the rotational level of an oxygen molecule in the ground electron state. The vector of the total momentum $\mathbf{J}$ of the molecule consists of the orbital momentum $\mathbf{N}$ and the molecular spin $\mathbf{S}$, $|\mathbf{S}| = \hbar$, where $\hbar$ is the reduced Planck constant. The quantum number J of the total angular momentum
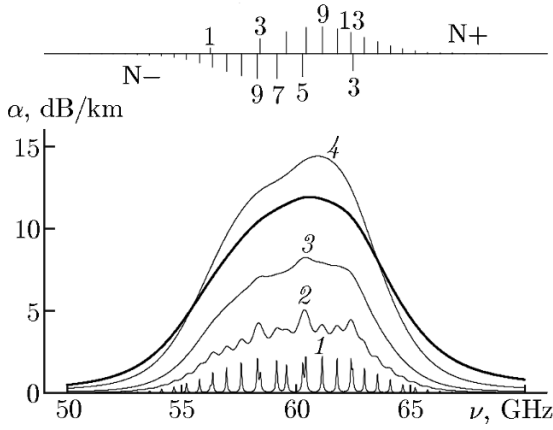
Fig. 1. Profile of the oxygen absorption band in atmospheric air at room temperature and pressures of 20, 200, 400, and 760 Torr according to the MPM with allowance for the collisional coupling effect (thin lines *1–4*, respectively). The absorption calculated by the sum of the Van Vleck—Weisskopf contours without allowance for collisional coupling effect under a pressure of 760 Torr is shown by a thick line. The positions and relative line intensities of both branches of the fine structure which form the band are marked by vertical lines on the top.

can take three values: $J = N+1$, $N-1$, and N, where N is the quantum number of the orbital momentum. Thus, spin-rotational interaction in the O_2 molecule splits each frotational level of the molecule into three sublevels, which are called the fine-structure levels. The spectral lines corresponding to transitions between these levels, according to the selection rules, merge into a broad band centered at about 60 GHz as the pressure is increased (see Fig. 1).

Among the transitions of the fine structure, two branches can be singled out. Formally, they are distinguished by the sign of the change in quantum number J: the transitions in which the total angular momentum decreases ($\Delta J = -1$, $\Delta N = 0$ or $J' \leftarrow J = N \leftarrow N + 1$) are denoted by $N+$ and the transitions with increasing total angular momentum ($\Delta J = +1$, $\Delta N = 0$ or $J' \leftarrow J = N \leftarrow N-1$), by $N-$, respectively. Figure 1 shows the oxygen band profile near 60 GHz in atmospheric air under a few pressures, calculated by the MPM (Millimeter-wave Propagation Model [9]), as well as the positions and relative intensities of the lines of the $N+$ and $N-$ branches. To demonstrate the contribution of the collisional coupling effect of the fine-structure lines, a band profile under atmospheric pressure, calculated as the sum of isolated lines without allowance for the collisional coupling (Van Vleck — Weisskopf contours) is also shown in Fig. 1.

The resonance lines of an oxygen molecule under low pressure look like isolated, but there is collisional coupling between them, which redistributes the absorption intensity between the lines whose profile overlap. Thus, the resulting profile of the band differs from the sum of the profiles of the constituting lines if they are assumed isolated. Compared with the sum of isolated line profiles, the real profile of the band is higher and narrower. This difference is stronger manifested when the pressure is increased. For example, under atmospheric pressure the difference of absorption at the band center is about 18% (see Fig. 1).

3.   THE MODELS THAT ALLOW FOR THE COLLISIONAL COUPLING EFFECT

The Van Vleck — Weisskopf contour, which does not allow for the collisional coupling effect [12], is classical for modeling of isolated lines of atmospheric molecules in the millimeter wavelength range. The expression for the absorption coefficient of the band when this contour is used has the following form:

$$\alpha(\nu) = \sum_i n\alpha_i \left(\frac{\nu}{\nu_{0_i}}\right)^2 \frac{1}{\pi} \left[\frac{\Delta\nu_i}{(\nu - \nu_{0_i})^2 + \Delta\nu_i^2} + \frac{\Delta\nu_i}{(\nu + \nu_{0_i})^2 + \Delta\nu_i^2}\right], \qquad (1)$$

where ν is the current frequency, ν_{0_i} is the center frequency of the ith transition, $\Delta\nu_i$ and α_i are the collisional half-width of the corresponding line at half-amplitude of the maximum and the integral intensity of the transition, respectively, and n is the density of oxygen molecules.

A general expression is known for the absorption coefficient stipulated by an arbitrary number of spectral lines [2]:

$$\alpha(\nu) = \frac{8\pi^3\nu n}{3hc}[1 - \exp(-\frac{h\nu}{kT})]\text{Im}[\text{Tr}(\rho\,\mathbf{dd}^T[\mathbf{I}\nu - \boldsymbol{\nu}_0 - ip\mathbf{W}]^{-1})], \qquad (2)$$

where ρ is the density matrix, $\mathbf{d}$ is the vector of the dipole moments of the transitions, $\boldsymbol{\nu}_0$ is a diagonal

matrix containing the frequencies of the corresponding transitions, $\mathbf{W}$ is the matrix of collisional interaction of the lines, p is the pressure, Tr is the trace of the matrix, and Im is the imaginary part.

The size of the matrix is determined by the number of lines taken into account. Profile (1) is a particular case of expression (2) for the diagonal matrix $\mathbf{W}$, i.e., where the collisional coupling of lines is absent.

The following was shown in [4]. If the coupling of lines is relatively weak, that is, the condition[1]

$$\left| \frac{pW_{lk}}{\nu_l - \nu_k} \right| \ll 1 \tag{3}$$

(here, the element W_{lk} of the collisional interaction matrix corresponds to the coupling between the lines l and k, and ν_l and ν_k are the frequencies of the corresponding lines) is valid, then expression (2) can be expanded in a series of powers of the pressure in terms of perturbation theory, and an analytical expression for calculation of the absorption coefficient of the band in the form of contributions of individual lines can be obtained with the insignificant terms neglected.

In the first approximation, the influence of spectral exchange on the profile of an isolated, collisionally broadened spectral line can be taken into account using one parameter Y, which is linearly dependent on pressure. This parameter characterizes the distortion of the line profile compared with the Van Vleck — Weisskopf profile, which is caused by the collisional coupling and is antisymmetric with respect to the center frequency. The corresponding model of the line contour is called the Rosenkranz model [4], and the absorption coefficient within the band is calculated as

$$\alpha(\nu) = \sum_i n\alpha_i \left(\frac{\nu}{\nu_{0i}} \right)^2 \frac{1}{\pi} \left[\frac{\Delta\nu_i + Y_i(\nu - \nu_{0_i})}{(\nu - \nu_{0_i})^2 + \Delta\nu_i^2} + \frac{\Delta\nu_i - Y_i(\nu + \nu_{0_i})}{(\nu + \nu_{0_i})^2 + \Delta\nu_i^2} \right], \qquad Y_i = y_i\, p, \tag{4}$$

where Y_i is the collisional coupling parameter. The latter can be determined experimentally for each line considered (i. e., it can be extracted from the line profile record) or calculated if the values of the elements of the $\mathbf{W}$ matrix are known. In a similar way, it is possible to obtain an analytical model of the line contour, which allows for the manifestation of the effect in the second order of pressure [3].

At present, the only model used in applications to calculate the coefficient of absorption of electromagnetic radiation by atmospheric oxygen in the millimeter and submillimeter wavelength ranges, is the MPM. This model takes into account the coupling between lines up to the first [9] and the second [10] orders of magnitude.

A more accurate and physically justified model is the one [7] developed on the basis of the ECS (Energy Corrected Sudden) formalism [2], in which absorption is calculated numerically by Eq. (2).

Analysis of the differences in the measured absorption coefficient and its value calculated using the ECS and MPM models has shown that at low temperatures the ECS model better corresponds to the experimental data, and at temperatures from 300 K and above, both models conform equally well to the measurement results at atmospheric pressure [7].

The main difference between the two models is as follows. In the ECS model, the absorption is calculated using Eq. (2) and empirically calculated matrix $\mathbf{W}$, while the MPM uses approximate methods that give analytical expressions for calculation of the absorption coefficient. The parameters of the individual lines used in these models can be compared in the following way [7]: the matrix $\mathbf{W}$ is calculated by the ECS method, then the collisional coupling coefficients of the first and second orders of magnitude, which are used in the MPM (calculation formulas are given in, e. g., [3]) are calculated from the matrix.

The empirical parameters of both models, which characterize the collisional coupling, were determined from the analysis of the oxygen and air absorption spectra obtained experimentally at atmospheric pressure, when the profiles of individual spectral lines merge into one common contour. The obtained sets of coefficients responsible for the collisional coupling of lines are not the only possible ones. This reflects

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[1] This is fulfilled for almost all lines of the 60-GHz oxygen band at pressures up to the atmospheric one.
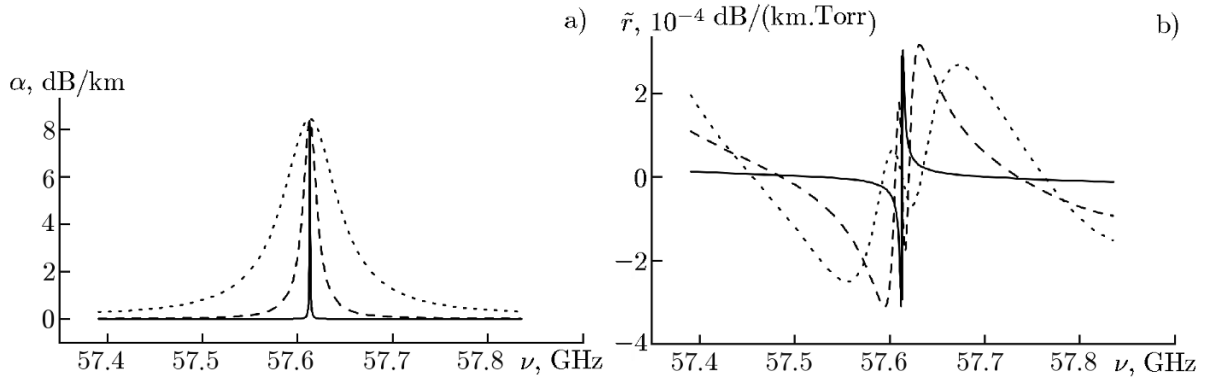
Fig. 2. Calculated profiles of the $N = 11-$ line at 296 K and different values of the oxygen pressure, which were found using the ECS model (a), and the pressure-normalized residuals $\tilde{r}$ of optimization of the model profile without allowance for collisional coupling (5) to calculated profiles (b). Solid lines correspond to a pressure of 0.25 Torr, dashed lines, to 5.00 Torr, and dotted lines, to 20.00 Torr.

the essence of the ill-conditioned solution of the inverse problem mentioned in the Introduction.

Observations at low pressures, from which one could estimate the contribution of the collisional coupling to the profiles of separate lines of the band and uniquely (within the experimental error) determine the values of the collisional coupling coefficients for each line, have not been performed to date.

Within the framework of this work, we numerically simulated the line profiles at low pressures. This allowed us to estimate the conditions under which the collisional coupling effect on the profile of a separate line can be detected, and conclusions can be drawn about the practical feasibility of such detection.

4.   NUMERICAL SIMULATION

To solve this problem, we first estimated the contribution of collisional coupling to the contours of individual lines of the band using the $N = 11-$ line as an example.

The absorption coefficient near the line center was calculated from the ECS model for a temperature of 296 K at pressures from 0.25 to 20 Torr in pure oxygen. Part of the calculated profiles is shown in Fig. 2a.

From the calculated profiles, it is necessary to subtract the contribution of all the remaining lines of the band. For this purpose, we used the MPM [10], because the ECS model does not allow for the contribution of each line separately. After that the model function, which does not allow for the coupling effect, was mathematically optimized to the refined profile "cleared" from the contribution of all other lines. The model function was the sum of the Van Vleck — Weisskopf profile and a quadratic function taking into account the possible inaccuracies in the subtraction of the contribution of other lines:

$$\alpha(\nu) = \alpha_0 \left(\frac{\nu}{\nu_0}\right)^2 \frac{1}{\pi} \left[\frac{\Delta\nu}{(\nu - \nu_0)^2 + \Delta\nu^2} + \frac{\Delta\nu}{(\nu + \nu_0)^2 + \Delta\nu^2}\right] + A(\nu - \nu_0)^2 + B(\nu - \nu_0) + C, \qquad (5)$$

where the intensity α_0, the center frequency ν_0, the linewidth $\Delta\nu$, and the parameters A, B, and C of the adaptive quadratic function are the varied parameters.

For a numerical estimation of the efficiency of optimization of model profile (5) to calculated profiles, we introduce the notion of "optimization quality." By the optimization quality we mean a ratio of the maximum absorption in the line profile to the r.m.s. deviation of the optimization residual (the optimization residual is the difference between the studied line profile and the model profile optimized to it). The estimator introduced in such a way will be similar to the signal-to-noise ratio for the same processing of experimental records. The optimization quality values obtained by processing of calculated profiles are given in Table 2. If the signal-to-noise ratio in the experimental recordings does not exceed the optimization quality value calculated under the same pressure, then the manifestation of the collisional coupling effect is unlikely to be detected. No experimental equipment known to us at present ensures the signal-to-noise ratio given in

Table 2 for the pressures indicated. This means that the characteristic systematic difference between the observed and the model profiles presented in Fig. 2b will be disguised by noise.

The collisional coupling effect can also be detected through indirect manifestations, for example, through systematic deviations of the line width and center frequency, which are obtained during the line profile processing, from the values calculated for the corresponding temperatures and pressures on the basis of the parameters measured experimentally in [8, 13] (called tabulated values for brevity's sake in what follows). Calculations by this method have shown that as the pressure is increased, the difference of the model profile optimization results from the tabulated values increases nonlinearly. Such a difference indicates that model function (5) does not conform to the profiles obtained. It appears that for the $N = 11-$ line at pressures of up to 20 Torr, deviations do not exceed 4 kHz for the line width and 60 kHz for the center frequency (see Fig. 3). Such deviations are less than the characteristic error of their determination from the experimental recordings obtained with modern spectrometers (see, e. g., [8] and references therein).

TABLE 2. Quality of optimization of the model profile (the minimum signal-to-noise ratio SNR_{min} required for the coupling effect detection) for the $N = 11-$ line and the $N = (13+, 3-)$ doublet as a function of pressure at a temperature of 296 K.

p, Torr	SNR_{min}, $N = 11-$	SNR_{min}, $N = (13+, 3-)$
0. 25	224000	206000
0. 50	115000	72000
0. 75	83000	41000
1. 00	63000	27000
2. 00	26000	10000
3. 00	16000	5800
5. 00	10000	3100
6. 00	9500	2700
8. 00	8200	2100
10. 00	7400	1900
12. 00	6600	1700
17. 00	5100	1500
20. 00	4400	1400

Thus, neither a direct nor an indirect method make it possible to detect manifestations of the collisional coupling for single lines of the 60 GHz band without a significant increase in sensitivity of the experimental apparatus.

The next step was the study of collisional coupling between the closely located lines (hereinafter "doublets"). Totally, among transitions of the fine structure of an oxygen molecule there are four such doublets: $N = (13+, 3-), (7+, 5-), (3+, 9-),$ and $(1+, 15-)$. Lines in each pair belong to different branches: one, to $N+$ and the other, to $N-$. Collisional coupling in the doublet should be stronger manifested because of the short distance between the line centers.

At atmospheric pressure, the condition of applicability of perturbation theory (3) to expression (2) can be violated for the doublets [14]. In the MPM, this does not lead to a problem, since the collisional coupling coefficients are calculated within the assumption that the elements of the $\mathbf{W}$ matrix which characterize coupling between the lines of the $N+$ branch and the lines of the $N-$ branch are equal to zero. Thus, the
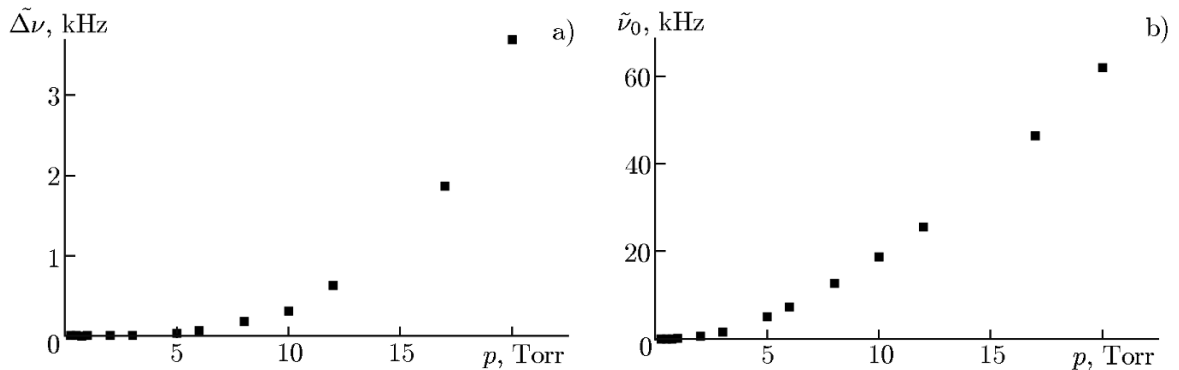

Fig. 3. Deviation of the width $\tilde{\Delta}\nu$ (a) and center frequency $\tilde{\nu}_0$ (b) of the $N = 11-$ line, obtained as a result of optimization of function (5) for the line profile calculated using the ECS model from the values obtained on the basis of tabulated data.
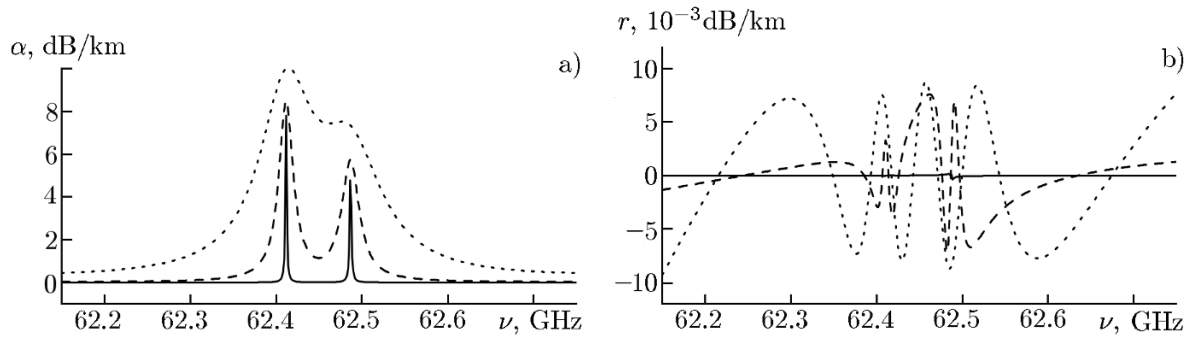
Fig. 4. Profiles of the $N = (13+, 3-)$ doublet at different pressures calculated using the ECS model (*a*) and the residuals r of optimization of the model profile without allowance for collisional coupling to calculated profiles of the $N = (13+, 3-)$ doublet (*b*). Solid lines correspond to a pressure of 0.5 Torr, dashed lines, to 6.0 Torr, and dotted lines, to 22.0 Torr.

left-hand side of Eq. (3) in the MPM also becomes equal to zero [14]. The ECS model is devoid of this feature since it uses direct semi-empirical calculation of the inverted matrix $\mathbf{W}$. Thus, if the $\mathbf{W}$ matrix, which is found with the help of the ECS model, is used, then at about an atmospheric pressure, condition (3) will be violated for the doublets. This means that applying the perturbation theory to Eq. (2) for calculation of absorption in the vicinity of doublets will be incorrect [7]. Nevertheless, at pressures two or three orders of magnitude lower than atmospheric, the condition of applicability of perturbation theory (3) should be fulfilled for doublets as well. In this case, the line profiles calculated within the ECS model should approximately correspond to the Van Vleck — Weisskopf model (1) and correspond well to the Rosenkranz model (4).

A doublet consisting of $N = (13+, 3-)$ lines was chosen for the study. The lines of this doublet, firstly, are located closer to each other in comparison with the other three doublets, secondly, they have a sufficient intensity, and, thirdly, their intensities differ insignificantly [5]. The above features make the $N = (13+, 3-)$ doublet a convenient object for experimental checking of the hypotheses put forward in this paper. Numerical analysis of the profiles of closely spaced lines was similar to the analysis of the manifestation of the collisional coupling effect for single lines of the band. Absorption in the region of the doublet was simulated at pressures of 0.5 to 22 Torr using to the ECS model (Fig. 4*a*). From the calculated value of the absorption coefficient, the sum of contributions from all other lines of the band calculated by the MPM was subtracted [10]. The resulting profile was optimized to the profile in the form of the sum of two Van Vleck — Weisskopf contours and a quadratic function (an analog of model (5)). The residuals of optimization for three different values of the pressure corresponding to the calculated profiles in Fig. 4 *a*, are given in Fig. 4*b*.

The values of the optimization quality of the model profile based on the Van Vleck — Weisskopf contours (similar to the values of the signal-to-noise ratio in experimental recordings) required for direct detection (i.e., detection by the characteristic form of the optimization residual) of the manifestation of the collisional coupling effect from experimental recordings are also presented in Table 2. They indicate that the signal-to-noise ratio required to detect the line coupling effect in a doublet at pressures of more than 10 Torr is closer to the actually achievable values, but still is very high for its direct observation.

As for the single line $N = 11-$, for the doublet $N = (13+, 3-)$ deviations of the line widths and center frequencies from tabulated values, which are related to the indirect manifestation of the effect, were calculated. The results for the three temperature values, 238, 258, and 298 K, are given in Fig. 5. As was expected, the effect increases with decreasing temperature. At pressures above 10 Torr, deviations, both in width and center frequency, begin to exceed fractions of a megahertz for both lines, which is larger than the usual statistical uncertainty of the values obtained during processing of experimental recordings.

Then we demonstrated that deviations of the line width and center frequency are due exactly to the collisional coupling, that was not taken into account in the model profile. For this, when the line widths
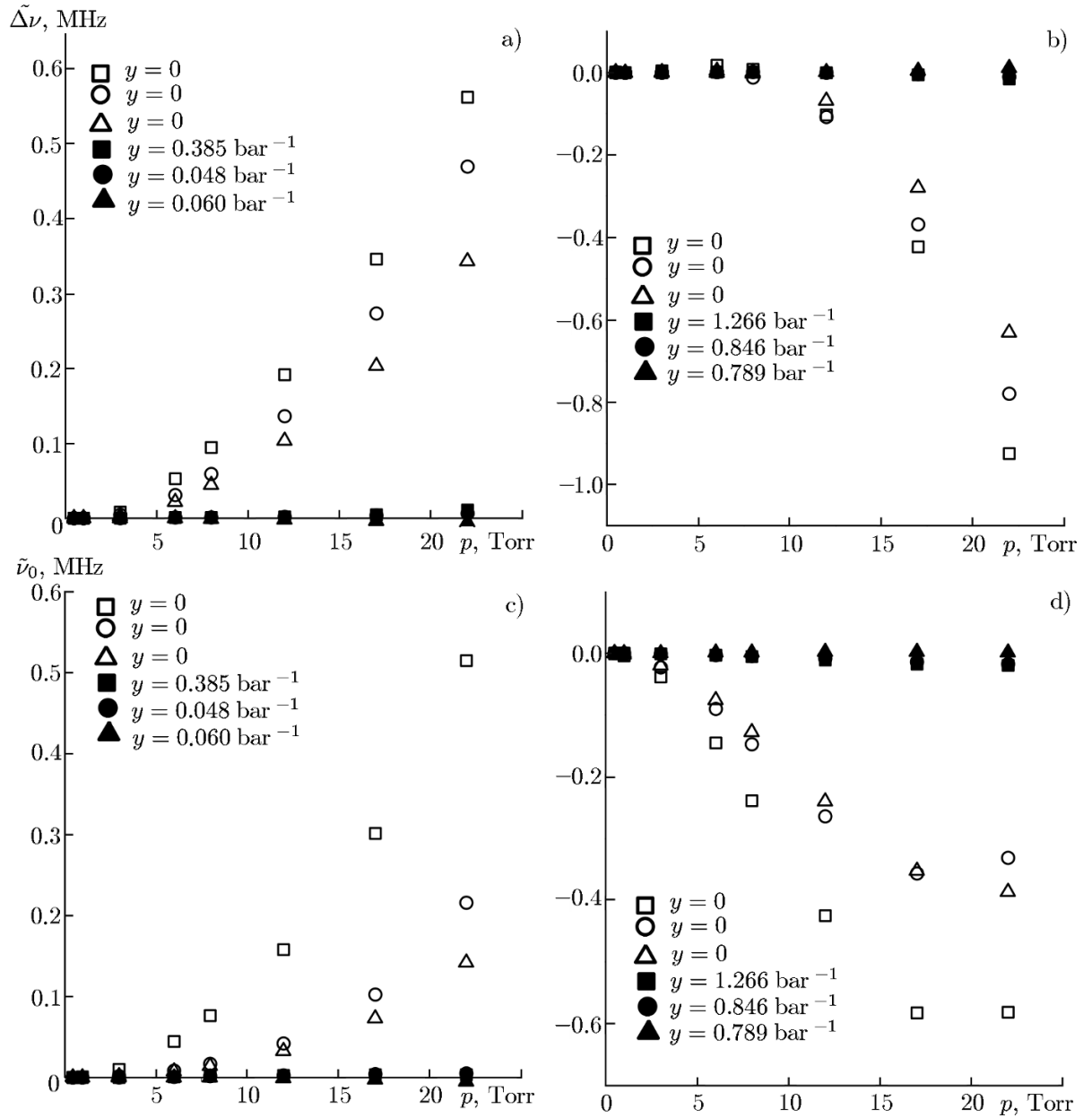
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Fig. 5. Deviations of the widths (*a* and *b*) and center frequencies (*c* and *d*) of the lines $N = 13+$ (*a* and *c*) and $N = 3-$ (*b* and *d*), which were obtained by processing of calculated profiles of the ECP model, from the values found from tabulated parameters [8]. Empty symbols show the deviations obtained by optimization of calculated profiles without allowance for collisional coupling and filled symbols show similar deviations obtained by optimization of the same profiles with allowance for collisional coupling. Square symbols correspond to a temperature of 238 K, round symbols, to a temperature of 258 K, and triangular symbols, to a temperature of 298 K.

and center frequencies were extracted from the model profiles calculated by the ECS method, the sum of the Rosenkranz profiles with fixed values of the collisional coupling parameters was used. These values were obtained by optimizing the same calculated ECS profiles to the Rosenkranz profiles, in which the intensities, center frequencies, line widths, and collisional coupling parameters, as well as the parameters of the additive quadratic correction which takes into account the possible inaccuracies in subtracting the contribution of the other lines (similar to profile (5)) were varied.

The values of the collisional coupling parameters Y extracted in such a way for both lines, as was

expected, depend linearly on the pressure, while the broadening coefficients and the center frequencies correspond to tabulated values, which made it possible to determine the collisional coupling coefficients y for both lines at different temperatures. That a model which takes into account the collisional coupling in the first order with the found coupling coefficients y not varied during optimization was applied to the calculated profiles reduced the deviation of the line widths and center frequencies from tabulated values (see Fig. 5). Within the statistical error of determination (comparable with the size of the symbols in Fig. 5), the widths of the doublet lines correspond to the tabulated values. Deviation of the center frequencies from tabulated values also decreased significantly, and only a weak systematic increase in the center frequency deviation, which is proportional to the pressure squared and corresponds in magnitude to the collisional coupling effect in the second order [10], remained. The quality of optimization increased by about 100 times compared to the optimization without allowance for collisional coupling.

Thus, the impact of the collisional coupling effect on the profile of the $N = (13+, 3-)$ doublet lines can be detected by an experiment. For a sufficient signal-to-noise ratio, a characteristic difference between the recorded profiles and the sum of the model Van Vleck — Weisskopf profiles will be tangible in the spectrum recording. With a lower sensitivity of the spectrometer, the collisional coupling effect will be manifested in the form of a systematic difference of the line parameters obtained in the experimental data processing from tabulated values.

5.   THE LINE PROFILE RECORDING PROCEDURE

The manifestations of the collisional coupling effect discussed in the previous section can be detected experimentally, for example, by using a spectrometer with radio acoustic detection of absorption (RAD), which permits quantitative studies of molecular spectra at higher pressures than the classical video spectrometers. The principle of operation, hardware features, and techniques for obtaining spectra with a RAD spectrometer used in this paper are described in detail in [15]. As the source of coherent continuous radiation, we used an OV-70 backward wave oscillator (BWO). The BWO frequency was stabilized by using a phase-locked loop (PLL) system [15, 16] by the harmonic of a microwave synthesizer with a frequency range of 2 to 20 GHz (Anritsu MG3692C), synchronized according to the rubidium frequency and time standard. The radiation intensity was modulated using a PIN modulator with a frequency of 180 Hz.

When the radiation passes through a gas-filled cell, into which a sensitive microphone is placed, the gas absorbs some of the radiation energy (if the radiation frequency is close to the frequency of the spectral line of the gas), is heated up and, expanding, deflects the microphone membrane. Diaphragm deflection is directly proportional to the radiation power and the absorption coefficient at the radiation frequency. Diaphragm oscillations at the modulation frequency are converted to an electrical signal, digitized by an analog-to-digital converter, and recorded for the further processing. The line is recorded step by step, scanning the radiation frequency of the synthesizer. To increase the sensitivity of the spectrometer, digital synchronous detection of the signal at the modulation frequency is employed.

The spectra in the vicinity of the lines 3− and 13+ doublet were recorded at pressures of 10.0, 14.7, and 19.2 Torr (the pressure 10 Torr was recorded by an MKS Baratron sensor with a guaranteed accuracy of about 0.25% and pressures above 10 Torr, by a Granville–Phillips sensor with a manufacturer-guaranteed accuracy of about 0.3 Torr) and temperatures of 238, 258, and 298 K (the accuracy of determination of the temperature by copper thermistors is ±0.5 K; the cell temperature stability was ensured by an automatic Julabo FP-50 HL thermostat within the accuracy of the temperature sensors).

There are two main hardware features that affect the form of the recorded lines. The first is that the radiation heats not only the gas, but also the elements of the gas cell, which leads to heating of the gas molecules colliding with them (hardware absorption). This heating, as the heating of a gas when it absorbs radiation, occurs with the modulation frequency of the BWO radiation. As a result, a spurious signal or a synchronous interference are added to the signal stipulated by absorption in the gas. The second problem consists of a quasiperiodic change in radiation power during the frequency scanning. This is due to the interference of the sounding radiation with unavoidable spurious reflections from the cell windows and the

elements of the waveguide channel in the spectrometer. Since the useful signal is proportional to the product of the absorption coefficient of the gas and the radiation power, the dependence of the radiation power on the frequency distorts the recorded molecular line profile, even if the hardware absorption is small.

When the single-line profiles are recorded, the pressure and related range of the BWO frequency tuning can always be chosen narrow enough to ensure that both the hardware absorption and the frequency dependence of the radiation frequency can be approximated by polynomials of no higher than the second order when the spectra are processed (the former is taken into account as an additive correction and the second, as a multiplicative correction in the model profile). In our case, this technique is not applicable, since at any pressure when two collisionally broadened lines spaced by about 70 MHz are recorded, the necessary range of the BWO frequency tuning is too broad. The range width exceeds half the period of the interference stipulated by the partial reflection of radiation between the windows of the cell and also between the input window and the BWO horn. Indeed, when the distance between the elements $L \approx 30$ cm, the characteristic period of the radiation power variation is $c/(2L) \approx 500$ MHz, where c is the speed of light in empty space.

In view of the foregoing, the hardware features of the RAD spectrometer were taken into account in this paper both at the stage of obtaining experimental data and at the stage of mathematical processing of recorded spectra. The hardware absorption spectrum was recorded when the cell was filled with a non-absorbing gas (nitrogen was used because of its molecular mass being close to oxygen, which provided an acoustic signal similar in magnitude at the same pressure), in the same frequency range, and with the same relative positions of the spectrometer elements as in the recording of oxygen doublets. The retrieved signal of the hardware function was subtracted from the experimental oxygen spectrum. The recording separated in this way from most of the synchronous interference was subjected to the further software "clearing" of the additional hardware absorption using the fact that the phases of the useful and spurious signals are different. This is due to the fact that there is a delay between the "useful" and "spurious" heating of the gas, the magnitude of which is determined by the geometry of the cell and the speed of sound propagation in the gas. The phase difference between the corresponding signals is constant at each pressure, although the amplitude of each of them is frequency dependent. Digital synchronous detection with two reference signals in quadrature to each other permits one, in principle, to select a detection phase such that the output signal will contain only a signal which is proportional to the absorption in the gas. The detection phase here is a variable parameter, the value of which is determined with allowance for the correspondence of the experimental profile to the calculated one. The procedure results in a partial loss of the useful signal, which is the greater, the closer the phase of the spurious signal to that of the useful signal.

In order to minimize the influence of the frequency-dependent multiplicative term on the profile of the doublet under study, each recording was repeated 10 times with a sequential moving of the cell along the radiation propagation axis with a step of about 0.5 mm. The recorded profiles were averaged. The total displacement corresponded to the wavelength of radiation at the center of the spectrum recording.

This procedure helps to a large extent to get rid of small-scale interference manifestations, but does not affect a smooth power variation over the entire range. The formula for determining the RAD spectrometer signal S at the frequency ν at a pressure p and temperature T can be written as follows:

$$S(\nu, p, T) = K(p, T)P(\nu, T)\alpha(\nu, p, T) + D(\nu, P, T), \tag{6}$$

where α is the desired absorption coefficient (information on the profile of the line that we extract from the recording), D is the contribution of the hardware absorption (it is eliminated by subtracting the hardware signal recorded in pure nitrogen and selecting the value of the detection phase), P is the radiation power in the cell, and K is the pressure- and temperature-dependent sensitivity of the cell [17]. The radiation power depends on both the frequency (an average smooth variation is taken into account) and the temperature (a temperature variation leads to a change in the relative positions of the elements, which changes the interference pattern and, as a consequence, the average radiation power). Thus, to obtain the desired
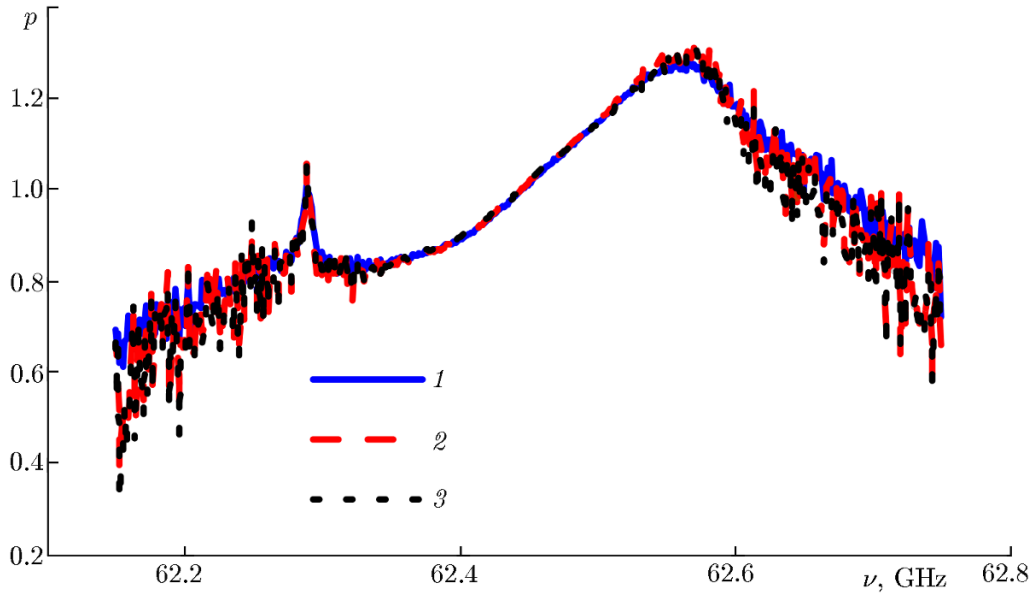
Fig. 6. Power $P(\nu)$ for the profiles recorded at a temperature of 298 K, which is normalized to the integral intensity of the doublet. Curve *1* corresponds to a pressure of 10.0 Torr, curve *2*, to a pressure of 14.7 Torr, and curve *3*, to a pressure of 19.2 Torr.

absorption profile corresponding to the form of the real dependence $\alpha(\nu)$ for given p and T, it is necessary to divide the experimentally recorded profile $S(\nu, p, T)$ by the dependence $K(p, T)P(\nu, T)$, which must be determined.

Assuming that the frequency dependence of the radiation power in the cell at the same temperature does not change when the gas pressure in the cell is varied (this is true up to differences in the refractive index, which are negligibly small under the experimental conditions), cross-processing of the data was used. If we assume that the "real" dependence $\alpha(\nu)$ is fairly close to the model, then dividing the signal magnitude $S(\nu)$ (6) by the calculated absorption coefficient $\alpha_{\mathrm{model}}(\nu)$ and taking into account the scaling factor K,[2] we must obtain a dependence close to to $P(\nu)$. All the dimensional quantities are taken into account in the coefficient K; therefore, $P(\nu)$ will be dimensionless. The average value of $P(\nu)$ should not be very different from unity, i.e., the function $P(\nu)$ is the normalized dependence of the average radiation power on frequency. The dependence $P(\nu)$ obtained from a recording at one pressure can be used to extract the dependence $\alpha(\nu)$ under any other pressure at a given temperature. For each temperature, the profile of the studied doublet was recorded at three different pressures. To extract $\alpha(\nu)$ from the spectrum recording at each of the three pressures, the averaged dependence $P(\nu$ obtained from two other recordings at the same temperature was used. Good coincidence of the $P(\nu)$ dependences obtained at one temperature from records at different pressures, as is demonstrated in Fig. 6, is evidence that the data processing was correct. It should be noted that the absorption coefficient decreases with frequency detuning from the center of the doublet to the wings, which leads to a signal drop, while the hardware noise does not change. As a result, when calculating $P(\nu)$ from the measured and calculated absorption coefficient there is a spread of values at the edges of the range.

6. EXPERIMENTAL DATA PROCESSING

The absorption profiles of the doublet $N = (13+, 3-)$ at three experimental pressures at a temperature of 238 K, obtained as a result of the primary data pre-processing described in the previous section,

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[2] This can be done, for example, by normalizing the calculated profile and an experimental recording to their integral intensity calculated as the area under the diagram of the corresponding profile.
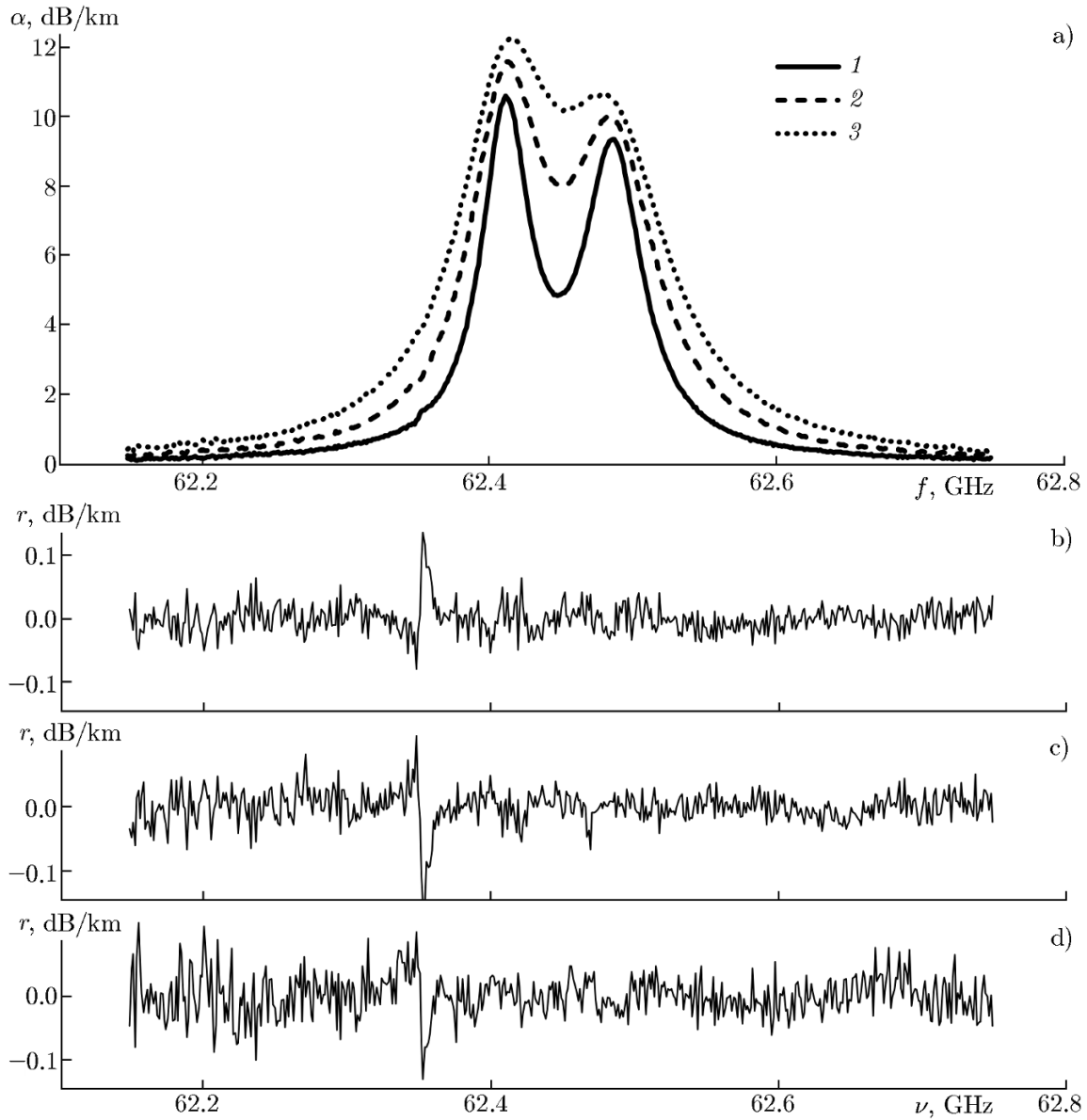
Fig. 7. Experimental oxygen spectra obtained using a RAD spectrometer for different values of pressure (*a*) and the residuals of optimization of these data to model profile (1) without allowance for the line coupling effect (*b–d*). Curve *1* on panel *a* and panel *b* correspond to a pressure a 10 Torr, curve *2* and panel *c*, to a pressure of 14.7 Torr, and curve *3* and panel *d*, to a pressure of 19.2 Torr.

and the result of their fitting to model (1) are shown in Fig. 7. A model similar to (5), which includes the two Van Vleck — Weisskopf profiles, was employed.

   The residuals of optimization of model function (1), which allows for the collisional coupling of the doublet lines to experimental recordings almost do not differ from noise. A small resonance near 62.4 GHz is an experimental artifact not related to absorption in oxygen, since its shape and width do not change when the pressure is varied. It appears that a model that does not take into account the interference effect describes experimental recordings up to the level of experimental noise. The absence of the effect in the form of the residual's systematic deviations similar to those shown in Fig. 4*b* is due to the fact that the signal-to-noise ratio achieved in the experiment turned out to be several times less than required for direct detection of the effect. For example, at a temperature of 238 K, the signal-to-noise ratio for recordings at pressures of 10.0, 14.7, and 19.2 Torr are 530, 450, and 290, respectively, while the values required for direct
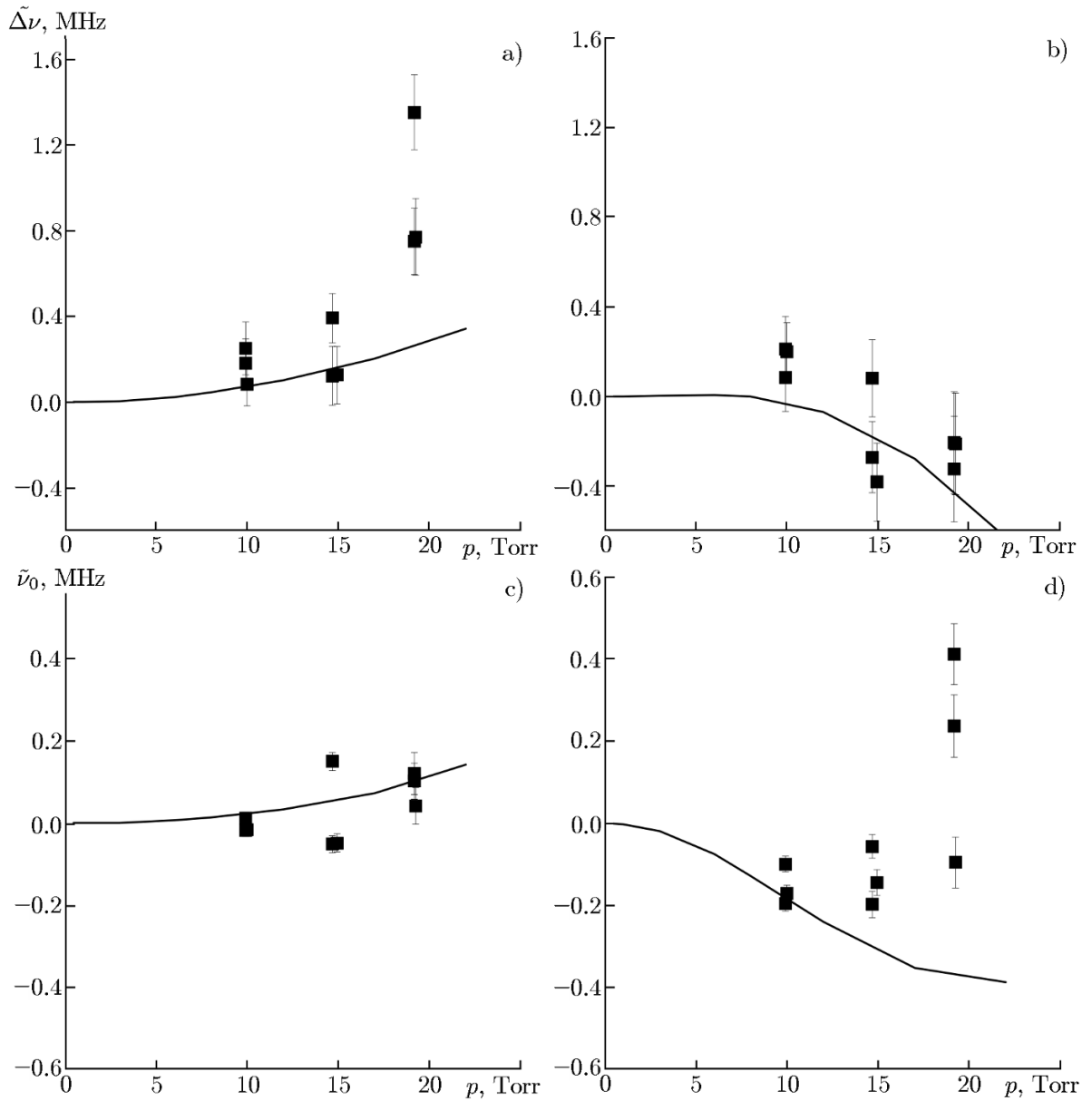
819

Fig. 8. Deviations of the widths (*a* and *b*) and frequencies (*c* and *d*) of the lines $N = 13+$ (*a* and *c*) and $N = 3-$ (*b* and *d*), which were obtained by processing of experimental spectra without allowance for collisional coupling, from the values calculated from tabulated parameters [8] (shown by dots with bars for the total error of determination) and similar deviations obtained by numerical simulation (shown by lines). The data are reduced to a temperature of 298 K.

observation of the collisional coupling, which were obtained in the numerical experiment, are equal to 1900, 1600, and 1400, respectively.

The results of an analysis of indirect manifestations of the coupling effect for the $N = (13+, 3-)$ doublet, which were obtained during processing of experimental recordings without taking into account the collisional coupling, are given in Fig. 8. The total error given in Fig. 8 consists of a statistical error of parameter determination during the model profile optimization and an error related to an instrumental error in measuring pressure and temperature. Deviations of the experimentally observed line widths (Figs. 8*a* and 8*b*) from tabulated values are similar in shape to the calculated deviations (the data of Fig. 5 are duplicated in Fig. 8 by lines), which can be considered as evidence for the coupling effect. Center frequency deviations from the tabulated value (Figs. 8*c* and 8*d*) also increase with increasing pressure, but the values obtained

TABLE 3. Values of the collisional coupling parameter y for the lines of the $N = (13+, 3-)$ doublet at a temperature of 296 K in pure oxygen.

	y, bar^{-1} ([8])	y, bar^{-1} ([3])	y, bar^{-1} (this paper)
$N = 3-$	-0.341	-0.216	-0.867
$N = 13+$	-0.369	-0.173	0.056

from experimental recordings poorly agree with the values found in the numerical simulation, which is especially notable for the $3-$ line. This can be due to the features of the model profile optimization to the experimental data: the variable parameter of the center frequency of the line is more sensitive to processing by the model with a large number of parameters, some of which correlate with each other.

Thus, a hypothetical indirect manifestation of the coupling effect of the lines of the $N = (13+, 3-)$ doublet is the experimentally observed deviation of the widths from the expected values obtained on the basis of measurements at pressures of up to 2–3 Torr [8], which increased nonlinearly at pressures of 10 to 20 Torr.

In order to ensure that the observed deviation of the line widths from tabulated values is due to the collisional coupling of the lines, we show that this deviation decreases when an adequate model function is chosen. For this, as in the case of the above-described numerical simulation of the profile of the $N = (13+, 3-)$ doublet, when extracting the line widths and center frequencies from experimental spectra in the model function, we replace the Van Vleck — Weisskopf contour by a Rosenkranz contour with a fixed value of the parameters Y.

Choosing the values of the parameters Y for the 13+ and 3− lines in pure oxygen is not easy. The values calculated theoretically in [3] were refined on the basis of experimental data in [8]. Another set of collisional coupling coefficients for the 13+ and 3− lines was obtained within the framework of this paper by optimizing the calculated profiles of the ECS model (Sec. 4) to the Rosenkranz model profiles. All these values of y are given in Table 3.

The use of the collisional coupling parameters given in Table 3 for the experimental data processing changes deviations of the extracted widths and center frequencies from the tabulated ones in comparison with the initial deviations obtained at $y = 0$. Nevertheless, due to the small amount of data and very significant experimental errors in measurement it cannot be said unambiguously which set of parameters leads to a better result. In addition, it should be borne in mind that an adequate description of the temperature dependence of the collisional coupling coefficient requires two parameters, y^0 and y^1 [10], since the temperature dependence of the collisional coupling coefficient has the form

$$y(T) = \left[y^0 + y^1 \left(\frac{T_0}{T} - 1 \right) \right] \left(\frac{T_0}{T} \right)^{0.8}. \qquad (7)$$

For two lines, it is needed to find a set of four parameters. As the most appropriate set of parameters, we chose the one that provided the smallest sum of the mean squares of deviations in the width and frequency of the lines under study from tabulated values. Selected values of the collisional coupling parameters were $y^0 = -0.12$ bar^{-1} and $y^1 = 0.25$ bar^{-1} for the 13+ line and $y^0 = -0.4$ bar^{-1} and $y^1 = 0.4$ bar^{-1} at $T_0 = 296$ K for the 13− line. Both parameters y^0 are negative, which is more consistent with the values used in the MPM than the values obtained when processing the calculated profiles of the ECS model.

Figure 9 shows deviations of the widths of the $N = (13+, 3-)$ lines from tabulated values, which were reduced to a room temperature. The values presented in the diagrams were obtained as a result of fitting of experimental recordings at all temperatures in cases where the collisional coupling effect was neglected (crosses) and was taken into account in the first order of pressure (squares) with the substitution of the chosen values of the parameters y given above. To demonstrate the trend of increasing deviation of the line width with the pressure, smooth curves of the form $y = ax^2$, approximating the line width deviations are shown (for each set of the line width deviations, a quadratic dependence on pressure with allowance for
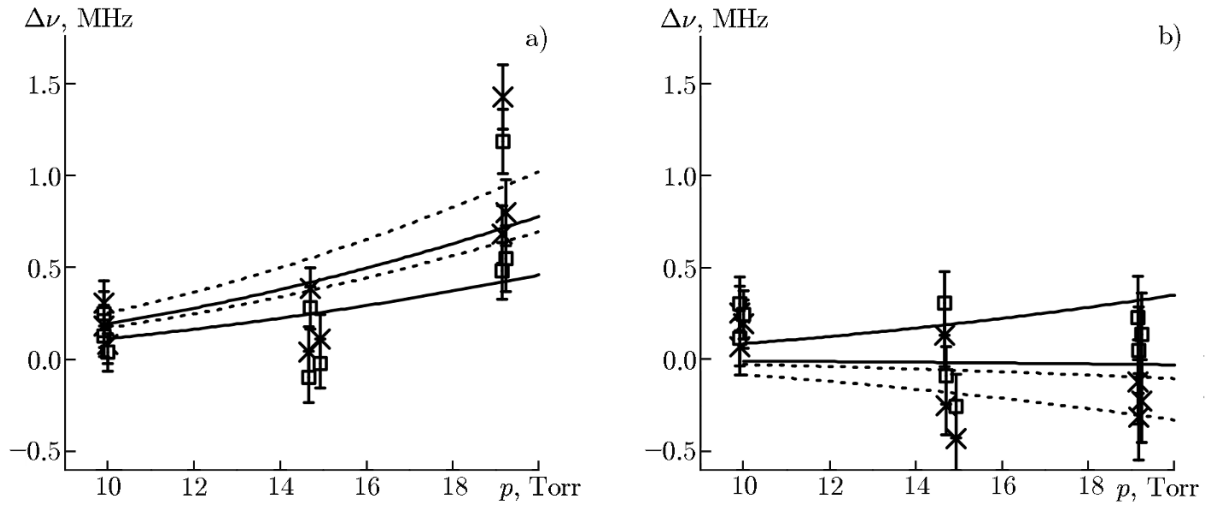
Fig. 9. Deviations of the widths of the $N = 13+$ (*a*) and $3-$ (*b*) lines from tabulated values reduced to a temperature of 296 K. Crosses denote the values obtained using the Van Vleck—Weisskopf contour and squares denote the values obtained using the Rosenkranz model. Smooth lines show the boundaries of the statistical uncertainty when the data are approximated by a quadratic function $y = ax^2$ (dashed lines correspond to the Van Vleck—Weisskopf model and solid lines, to the Rosenkranz model).

the statistical error of determination of the parameter a is shown). It can be seen that allowance for the collisional coupling reduces deviations of the line width from the tabulated value by an amount comparable with the statistical error of determination of the deviation. The difference in the deviations of the center frequencies of the lines when the model is changed almost does not manifest itself, apparently because the systematic errors in determining the frequency due to inaccurate accounting for the hardware function exceed the deviation related to the line coupling effect.

7. CONCLUSIONS

Using numerical simulation, it was shown that the collisional coupling effect can indirectly manifest itself during processing of experimental data in the form of a systematic deviation of the line widths and center frequencies from tabulated values. As was expected, allowance for the collisional coupling in the first order of pressure using model (4) with fixed values of y puts the parameters extracted from model profiles into correspondence with tabulated ones. When analyzing the experimental recordings of the profile of the (13+, 3−) doublet in the same way, a systematic deviation in line widths from tabulated values with the model profile not allowing for the collisional coupling was demonstrated. When the collisional coupling is taken into account, the deviations decrease, which can be used for the experimental determination of the coupling parameters of the lines. The accuracy of determination of the parameters is governed by the signal-to-noise ratio of the experimental data.

Thus, it can be concluded that exactly the collisional coupling effect (which with chosen pressures, can be taken into account in the form of first-order corrections) was revealed during processing of experimental records. Another result of the work is the estimation of the signal-to-noise ratio required for detection of collisional coupling in the absorption lines constituting the 60 GHz oxygen absorption band. The magnitude of this ratio determines the spectrometer sensitivity that is needed to achieve for such a detection.

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