SPECTROSCOPY OF ATOMS
AND MOLECULES

Modeling of the Profile of the 60 GHz Absorption Band of Atmospheric Oxygen Using the Memory Function Formalism

D. S. Makarov[a], N. N. Filippov[b], and M. Yu. Tret'yakov[a]

[a] *Institute of Applied Physics, Russian Academy of Sciences, Nizhni Novgorod, 603950 Russia*
[b] *St. Petersburg State University, Peterhof, St. Petersburg, 198504 Russia*

Received January 16, 2008

Abstract—The profile of the oxygen absorption band centered at 60 GHz is modeled using the formalism of memory functions. The memory function determines a relation between the initial and final states of a molecule after its collision. The model profile takes into account the spectral exchange and contains two parameters, which depend on temperature and pressure. These parameters characterize the probabilities of spectral exchange between series of lines (branches) corresponding to molecular transitions of different types. To describe the absorption profile in the frequency range from 0 to 120 GHz in terms of the model proposed, the "+" and "–" branches of fine structure transitions and the series of nonresonance lines with frequencies on the order of 10^{-3}–10^{-5} GHz are taken into account. The values of the parameters that take into account the spectral exchange are found from the condition of the best fit between the developed model profile and the profile calculated according to the millimeter-wave propagation model. The parameters found have physically substantiated and smooth temperature dependences, which confirms the adequacy of the model. The difference between these modeled does not exceed 2–3%, which corresponds to the declared uncertainty.

INTRODUCTION

Advantages in spectroscopy of the millimeter–submillimeter range make it necessary to gain a deeper insight into the conditions of propagation of radio waves of this range in the Earth's atmosphere and to construct exact models describing this process.

To model the absorption of radiation in a gas mixture at arbitrary pressure and temperature in a certain frequency range, for each spectral line of all the molecular components of the mixture, one needs to know such parameters as the central frequency, the intensity, and the coefficients of pressure-induced broadening and shift of the line (including the pressure of buffer gases), as well as the temperature dependences of all these parameters. In addition, in the majority of cases, it is necessary to somehow take into account the nonadditivity of line contours upon their overlap (the effect of interference of lines) [1, 2].

The millimeter absorption spectrum of the oxygen molecule is caused by magnetic dipole transitions in the $^3\Sigma$ electronic state [3, 4]. The total momentum of the molecule $\mathbf{J} = \mathbf{N} + \mathbf{S}$, where $\mathbf{N}$ is the rotational momentum, and $\mathbf{S}$ is the spin of electrons of the outer shell. Since, for the oxygen molecule, $S = 1$, then, according to the momentum addition law upon spin–orbit interaction [5], the quantum number J of the total angular momentum can acquire the following three values: $J = N, N \pm 1$ (where N is the quantum number of the rotational momentum of the molecule). The number N acquires only odd values, since the nuclei of the oxygen molecule are identical, and their spin is zero. For each triplet with a characteristic value of N, according to the selection rules ($\Delta N = 0$, $\Delta J = \pm 1$), there are only two allowed transitions of the fine structure. One of them is the transition $N, J \longrightarrow N', J' = (N, N - 1) \longrightarrow (N, N)$, which is denoted as $N-$. The other transition is $(N, N + 1) \longrightarrow (N, N)$, and it is denoted as $N+$. Mainly, all these lines fall into narrow band near 60 GHz, whereas the line 1– is located separately at a frequency of 118.75 GHz (since this line is isolated and has a small absorption coefficient at the maximum, no more than 2 dB/km, it is frequently used in various applied problems).

Van Fleck was the first who described the spectrum of molecular oxygen in the atmosphere [6]. Since the first laboratory [7, 8] and field [9, 10] experiments, interest in studying the millimeter spectrum of oxygen has only increased, and experimental and theoretical investigations performed have resulted in creating a millimeter-wave propagation (MWP) model [11] and in its refining [12].

The MWP model describes the band line by line. The effect of interference of lines is taken into account in the first order of smallness with respect to the pressure with the help of an additional parameter that characterizes an asymmetric distortion of the profile for each spectral line. The MWP model takes into account about 40 lines of the fine structure of oxygen, which

means that the model uses the same number of the interference parameters. These parameters are determined from variational mathematical calculations using experimental data on the absorption profile at various pressures. It is clear that, under such an approach, the obtained values of these parameters correlate with each other and with other parameters of lines (first of all, with the broadening coefficients and amplitudes, as was indicated by the authors of [12]). Therefore, the question arises as to whether the parameters can be exactly determined.

A need in a new model transpires from the fact that high-precision measurements of the absorption profile of the 60 GHz band performed in [13] showed that the MWP model fails to describe the profile observed up to experimental noise. Formally, the difference between the data of the MWP model and experiment is analogous to a correction that takes into account the effect of interference of lines in the second order. This correction was calculated as early as in 1981 [14].

We believe that the introduction of additional parameters that take into account second-order interference effects in the MWP model will not provide an adequate solution to the problem. An alternative approach is the use of other methods of description of absorption bands such that they make it possible to considerably reduce the number of empirical parameters of the model [1].

In this work, we present the model that describes the absorption of radiation in the 60 GHz band of oxygen under atmospheric conditions and that is constructed according to the same principles as the model of [1]. The model takes into account the interference effect with the help of two variable parameters for constant temperature and pressure values. We compare the model presented with the MWP model and with experimental data and estimate the correlation of parameters that take into account the interference effect.

MODELING OF THE ABSORPTION PROFILE

A representation of the absorption profile of a band consisting of many lines as a sum of the profiles of individual lines is true only if the lines do not overlap. Experimental studies of spectral bands consisting of many closely crowded lines at subatmospheric pressures or higher show that the description of the band profile as a sum of the profiles of individual lines is inexact [1].

The frequency dependence of the absorption coefficient of a molecule is determined by the Fourier transform of the autocorrelation function of the dipole moment of the molecule [15]. The correlation function can be constructed by various methods that take into account collisional interactions of molecules, which cause the effect of interference of lines.

Thus, the collisional interaction can be described by a so-called relaxation matrix [16], whose form completely determines the shape of the band. The diagonal elements of this matrix determine the band shape without taking into account the interaction, and the off-diagonal elements are responsible for nonadditive distortions of overlapped lines (the indices of the matrix denote the transitions that form the band under consideration).

If only the diagonal elements of the matrix are taken into account, the spectral function takes the form of the sum of Lorentz profiles, with the real and imaginary parts of the diagonal element being numerically equal to the width and the shift of the corresponding line, respectively. The off-diagonal elements can be used, for example, for the calculation of the first-order interference parameters in the Rosenkranz profile [16, 17].

Although the knowledge of the interaction matrix yields complete information on collisions, the calculation of the relaxation matrix is a very complicated problem. It is commonly solved using various approximations and simplifications for both the interaction potential and the trajectories of molecules [18]. At the same time, there are also semiempirical methods of modeling of the absorption profile taking into account the interference effect of spectral lines. One such method is the formalism of memory functions [1, 19, 20].

The time evolution of the correlation function $C(t)$ can be described by the following relation:

$$\dot{C}(t) = -\int_0^t K(t')C(t-t')dt'. \tag{1}$$

The kernel of the integral operator $K(t')$ is termed the memory function. By Fourier transforming relation (1) and applying simple algebra, we obtain

$$\tilde{C}(\omega) = C(0)/[i\omega + \tilde{K}(\omega)]. \tag{2}$$

Expression (2) has the general character, and the main part is played here by the Fourier transform $\tilde{K}(\omega)$ of the memory function. There are simple, physically substantiated, and, in many cases, exact methods for its construction. Initially, we write the memory function in the absence of collisions,

$$C_0(t) = \sum_m A_m e^{i\omega_m t}, \quad C_0(0) = \sum_m A_m = A_\Sigma,$$

where A_m are the intensities of spectral lines that are taken into account upon construction of the model, and ω_m are their central frequencies.

Then, the Fourier transform of the memory function is

$$\tilde{K}_0(\omega) = -i\omega + A_\Sigma/\tilde{C}_0(\omega).$$

Taking into account the Poisson distribution, the probability of n collisions during the time t is written as
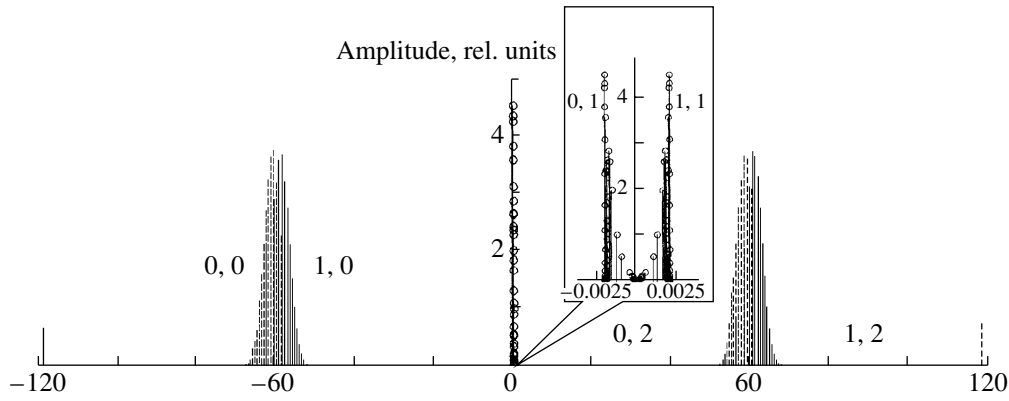
$$P_n(t) = (1/n!)(t/\tau)^n \exp(-t/\tau), \tag{3}$$

Fig. 1. Series of absorption and emission lines of the oxygen molecule used in the construction of the model. The figures are the values of (n, q).

where τ^{-1} is the characteristic collision frequency.

Assume that a molecule that underwent the first collision be in a state that is only determined by the statistical weight of the final state and be in no way dependent of the state of the molecule before the collision (the approximation of strong collisions). From the viewpoint of the memory function, this means that, at the moment of the collision, this function becomes zero. Then, using expression (3) for the calculation of the probability of absence of collisions, we can write

$$K(t) = K_0(t)P_0(t) + 0 \times (1 - P_0(t))$$
$$= K_0(t)\exp(-t/\tau). \qquad (4)$$

By substituting Fourier transform (4) into the expression for C_0 and performing simple transformations, we obtain

$$\tilde{C}(\omega) = \frac{\tilde{C}_0(\omega - i\tau^{-1})}{1 - \tau^{-1}\tilde{C}_0(\omega - i\tau^{-1})/A_\Sigma}.$$

The spectral function

$$F(\omega) = \operatorname{Re}\tilde{C}(\omega)/\pi,$$

constructed in the approximation of strong collisions, does not contain any parameters that affect the interference effect. The approximation of strong collisions is an idealized notion of the change in the state of a molecule as a result of the collisional interaction. Analysis of relaxation matrices calculated by various methods makes it possible to correct the construction of the correlation function. Thus, it was shown in [16] that matrix elements corresponding to the mutual influence of spectral lines belonging to different branches (for example, belonging to the P and Q branches of vibrational–rotational transition series) are smaller than matrix elements corresponding to the mutual influence of spectral lines of one and the same branch.

As was mentioned above, the oxygen absorption band under investigation also contains two branches of

transitions that differ in the sign of change in the quantum number J, which were denoted as $N+$ and $N-$. Consequently, for the model under construction to be more adequate, it should take into account the weakening of the interbranch interaction compared to the intrabranch one. Another idealized approximation is the approximation of independent branches. This approximation assumes that branches do not interact and that, within each branch, the interaction is assumed to occur in the strong-collision approximation.

To correctly construct the correlation function for the oxygen absorption band under investigation, we recall the transitions that occur in the frequency range up to 120 GHz. First, these are the above-mentioned fine structure transitions in the $^3\Sigma$ state, whose parameters were studied in [13]. Second, it is necessary to take into account one more series of lines, which appreciably contribute to the spectral function. This is the series of the so-called nonresonance transitions that occur as a result of a change in the orientation of the total momentum of the molecule in the space. The central frequencies of these lines are close to zero, and their intensities are several orders of magnitude lower than the intensities of the fine structure lines. Nevertheless, their contribution to the spectral function is on the order of A_m/ω_m^2, which is comparable with the contribution from the fine structure lines (Fig. 1). Apart from the fine structure transitions and nonresonance transitions in the absorption spectrum, it is also necessary to additionally take into account analogous transitions in the emission spectrum. We will them as lines with negative central frequencies, which are equal in magnitude to the central frequencies of analogous absorption lines.

Now, we separate collisions into three types,

$$\tau^{-1} = \tau_1^{-1} + \tau_2^{-1} + \tau_3^{-1},$$

where

$$\tau_3^{-1} = C_{SC}\tau^{-1}; \quad \tau_2^{-1} = (1 - C_{SC})C_{BR}\tau^{-1};$$

$$\tau_1^{-1} = (1 - C_{SC})(1 - C_{BR})\tau^{-1}.$$

Here, τ_1^{-1} is the frequency of collisions that cause interactions within an individual branch ($N+$, $N-$, or nonresonance lines); τ_2^{-1} is the frequency of collisions that cause interactions between nearest branches; τ_3^{-1} is the frequency of collisions causing interactions between all the branches; C_{SC} and C_{BR} are the coefficients that characterize the number of particular collisions in the total number of collisions per unit time. The interactions within and between branches are still assumed to be strong, but the characteristic collisional frequency in the correlation function proves to be corrected.

For the construction of the correlation function to be more convenient, we will enumerate the branches with two indices (n, q) as is shown in Fig. 1.

Preliminarily, we introduce the notation

$$A_\Sigma^{nq} = \sum_{\substack{m \\ n, q = \text{const}}} A_m, \quad A_\Sigma^q = \sum_{\substack{n \\ q = \text{const}}} A_\Sigma^{nq}, \quad A_\Sigma = \sum_q A_\Sigma^q.$$

The correlation function that takes into account the interactions of lines in each individual branch is written as

$$C_0^{nq}(\omega) = \sum_{\substack{m \\ n, q = \text{const}}} A_m/[i(\omega - \omega_m) + \tau^{-1}],$$

$$C_1^{nq}(\omega) = C_0^{nq}(\omega)/[1 - \tau_1^{-1}C_0^{nq}(\omega)/A_\Sigma^{nq}].$$

The correlation function that takes into account the interactions of branches with the same index q is written as

$$C_0^q(\omega) = \sum_{\substack{n \\ q = \text{const}}} C_1^{nq}(\omega),$$

$$C_1^q(\omega) = C_0^q(\omega)/[1 - \tau_2^{-1}C_0^q(\omega)/A_\Sigma^q]$$

Finally, the correlation function that takes into account the interactions between all branches has the form

$$C_0(\omega) = \sum_q C_1^q(\omega),$$

$$C_1(\omega) = C_0(\omega)/[1 - \tau_3^{-1}C_0(\omega)/A_\Sigma].$$

The parameter τ^{-1} was determined from the condition of equality of the average linewidths Δv_m^{exp} calculated from experimentally determined broadening coefficients and model linewidths Δv_m^{mod},

$$\sum_m A_m\Delta v_m^{\text{mod}} = \sum_m A_m\Delta v_m^{\text{exp}},$$

where

$$\Delta v_m^{\text{mod}} = \tau^{-1}[1 - (1 - C_{SC})(1 - C_{BR})A_m/A_\Sigma^{nq}$$

$$+ (1 - C_{SC})C_{BR}A_m/A_\Sigma^q + C_{SC}A_m/A_\Sigma].$$

Accordingly, a correction term aimed at minimizing small differences in the m dependences of Δv_m^{mod} and Δv_m^{exp} was introduced into the spectral function,

$$F(\omega, C_{BR}, C_{SC})$$

$$= \frac{1}{\pi}\text{Re}\, C_1(\omega)\frac{\displaystyle\sum_m A_m\Delta v_m^{\text{exp}}/[(\Delta v_m^{\text{exp}})^2 + (\omega - \omega_m)^2]}{\displaystyle\sum_m A_m\Delta v_m^{\text{mod}}/[(\Delta v_m^{\text{mod}})^2 + (\omega - \omega_m)^2]}.$$

Therefore, the absorption profile is described by the following function:

$$\alpha(\omega, C_{BR}, C_{SC}) = A\omega^2 F(\omega, C_{BR}, C_{SC}), \qquad (5)$$

where A is a normalization amplitude coefficient.

As a result, we obtained the expression for the absorption profile, which takes into account the line interference effect with the help of two parameters that characterize the fraction of collisions causing particular interactions from the total number of collisions per unit time. Analogously to [12], the amplitude factor A is calculated using the intensities of lines of considered bands and the data on the composition of the atmosphere and on the oxygen isotope abundance, as well as the populations of the ground vibrational state.

The objective of this work is to describe the absorption profile of atmospheric oxygen. As known, such parameters of atmospheric air as pressure and temperature vary in wide limits. The pressure varies in the range from 0 to 760 Torr, and the temperature varies from –60 to +60°C. To describe the absorption profile at any pressure and temperature from these intervals with the help of the constructed function, which depends on two parameters that characterize the interference of lines, we should determine the dependences of these parameters on the pressure and temperature. Apart from these two parameters, we also need to know the amplitudes, the central frequencies, and the broadening coefficients of all the lines used in the model, as well as the temperature dependences of these parameters.

The central frequencies of the lines of the fine structure (up to $N = 27\pm$) and their coefficients of broadening induced by the oxygen and nitrogen pressures were
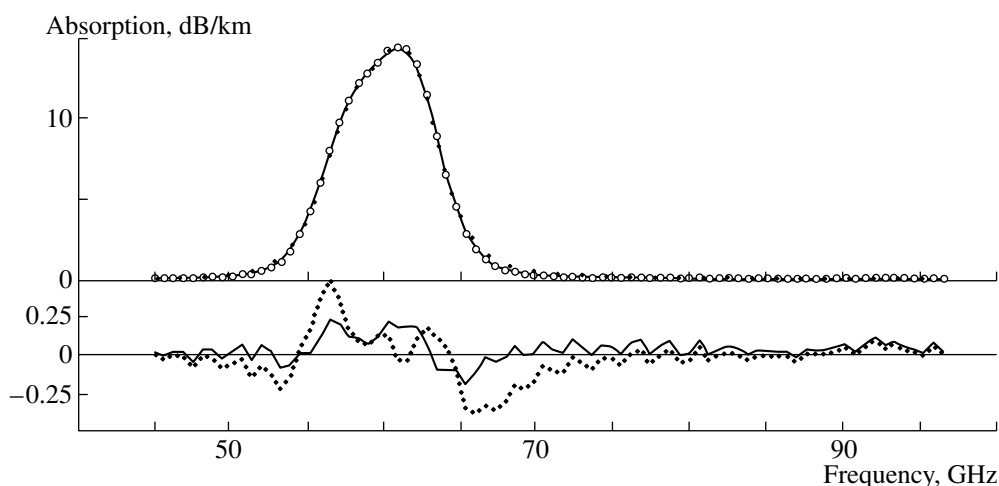
Fig. 2. Top: (circles) experimentally determined absorption profile of the oxygen molecule at 755 Torr and 22°C, (solid curve) absorption profile calculated by the MWP model, and (dots) absorption profile constructed with our model. Bottom: deviation of the experiment from the MWP model (solid curve) and from the new model (dotted curve).

experimentally determined in [13] with a high accuracy. The broadening parameters of the lines that were not measured but that were also taken into account in the MWP model (up to $N = 37\pm$, which is the maximal value of N that appreciably contributes to the absorption profile) were determined by extrapolation. The intensities of the lines of the fine structure were taken from the HITRAN database (version of 2007) [21]. The calculation of the temperature dependences of intensities is straightforward [3]. The temperature dependences of the air-induced broadening coefficient were the same as in [12]. All the parameters of nonresonance lines were also taken from the HITRAN database.

Therefore, with the parameters of the nonresonance lines and the lines of the fine structure previously being determined by particular methods, function (5) becomes the model function for the description of the absorption profile of the band centered at 60 GHz.

ANALYSIS OF THE NEW MODEL

Figure 2 compares the model profiles calculated by the MWP model [12] and by our model with the experimental data of [13]. The experimental profile was measured in the atmospheric air at 755 Torr and 22°C. The parameters C_{BR} and C_{SC} in model profile (5) were assumed to be variable and were determined from the regression of the model function to the experimental data with the help of standard programs. The bottom of Fig. 2 presents the deviations of the experimental data from the MWP model profile and from our model function (5). It is seen that both residuals depend on temperature in a complicated way and are on the same order of magnitude. It is also seen that the residual of the new model is still somewhat greater than the residual of the MWP profile. At the same time, with an insignificant loss in accuracy (how far the new model is indeed

behind in accuracy can be clarified only from analysis of a great body of experimental data), the number of the parameters of the model is significantly reduced. The new model was constructed without using an expansion in a power series of any small quantity. Only physically substantiated data on collisions in the gas were used. At the same time, we assumed that the desired effect is achieved as a result of only one collision; however, strictly speaking, it results from several collisions. This assumption introduces into the model profile the most appreciable deviations from the real profile, provided that the remaining parameters of the lines were determined exactly. It is clear that further improvement of the model is indeed connected with the method of taking into account the effect of collisions.

Despite the fact that the model has only two variable parameters, it is necessary to estimate their mutual correlation. To this end, we performed the following numerical experiment: we fitted the constructed model function (5) to the sum of the profile constructed with the help of the same function (with the fixed values of the parameters C_{BR} and C_{SC}) and various realizations of the Gauss noise with a fixed dispersion. The results of this numerical experiment are presented in Fig. 3 as a plane of the parameters C_{BR} and C_{SC} and in Fig. 4 as a probability distribution of each of these parameters.

The obtained value $R = 0.36$ of the coefficient of the mutual correlation of the parameters of the model indicates that they weakly depend on each other. Apart from the small value of the correlation coefficient, it should be also noted that the relative dispersion of the parameters exceeds the relative dispersion of the noise used in the numerical experiment (2–3% from the maximal absorption coefficient). This indicates that the response of the model to a change in the parameters is not very strong, which, in some cases, impedes exact determination of the parameter upon fitting of the
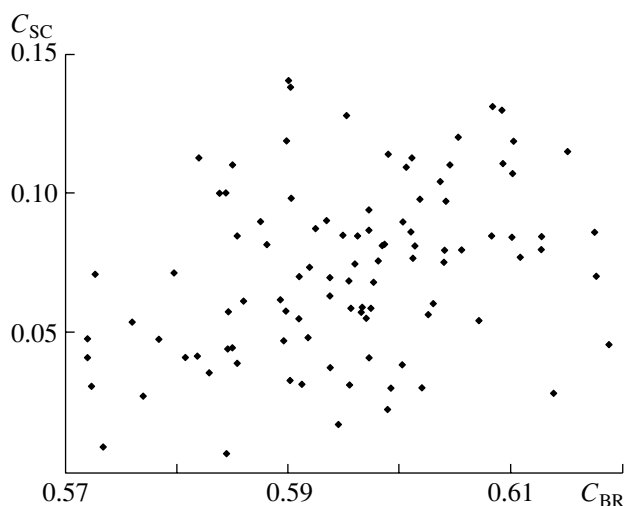
Fig. 3. Joint distribution of the parameters C_{BR} and C_{SC} on the plane upon statistical analysis of their mutual correlation.
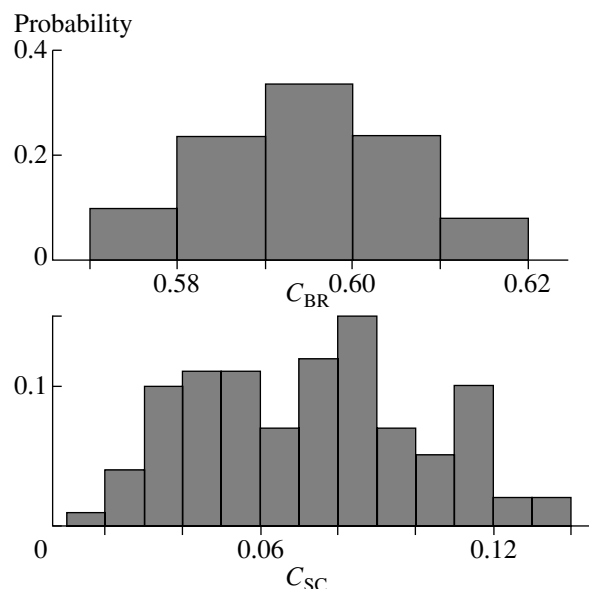

Fig. 4. Probability distributions of the parameters C_{BR} and C_{SC} upon statistical analysis of their mutual correlation.
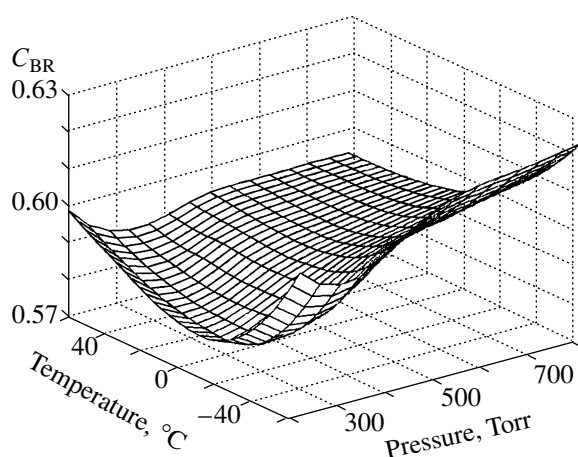

Fig. 5. Dependence of the parameter C_{BR} on the temperature and pressure.
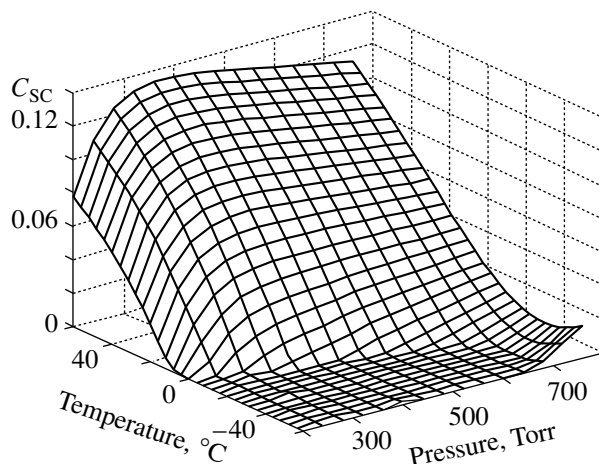

Fig. 6. Dependence of the parameter C_{SC} on the temperature and pressure.

model profile to the experimental one. At the same time, this same effect makes it possible to smooth the temperature dependences of the parameters in ranges where they cannot be determined with a sufficient accuracy without losing the accuracy of the model profile.

The parameters C_{BR} and C_{SC} characterize the type of collisions and, by virtue of their physical meaning, should not depend on the frequency of collisions, i.e., on the pressure. However, to increase the description accuracy of experimental data, we will assume in what follows that the model contour of the band has only an approximation character and that these parameters depend not only on the temperature but also on the pres-

sure of the gas. To determine the dependences of the parameters C_{BR} and C_{SC} on the temperature and pressure, a certain number of experimental measurements of the absorption in the entire range of temperatures and pressure of interest are necessary.

Since such data are not available at present, and because their obtaining requires considerable material resources and working time, to test the validity of the approach proposed, we decided to use in their place the profiles calculated by the MWP model.

This can be substantiated by the following considerations. The parameters of the MWP model are based on the experimental data obtained for the temperature

range 6–54°C and for pressures from a few Torr to 1 atm [12]. The values of the MWP parameters for a wider temperature range are determined by extrapolation of experimental dependences. It is known that the accuracy of this model is about 2–3% [12].

Therefore, by fitting our model function to MWP profiles at different temperatures and pressures, we can obtain the temperature and pressure dependences of the parameters C_{BR} and C_{SC}.

The dependences obtained are shown in Figs. 5 and 6. It is seen that the pressure dependences of the two parameters are nonlinear, which also indicates that it is necessary to further improve the model, which, at this stage, is still approximate in character.

CONCLUSIONS

We proposed a physically substantiated method for describing the absorption profile of the oxygen molecule near 60 GHz taking into account interference of lines, which is based on the memory function formalism. As fixed parameters, the new model uses the experimental data on lines of the band under investigation. The interference effect at certain pressure and temperature values is taken into account with the help of two additional variable parameters for the entire absorption band. The temperature and pressure dependences of the additional parameters of the new model were obtained. All these dependences are smooth, which indicates that the description proposed is adequate.

To evaluate the accuracy of the new model, its results were compared with experimental data. This comparison shows that the accuracy of the new model is almost as high as the accuracy of the widely used MWP model, which, in view of the fact that the number of additional parameters in the new model was reduced by an order of magnitude, also indicates that the model developed is adequate.

ACKNOWLEDGMENTS

REFERENCES

1. M. V. Tonkov, N. N. Filippov, Yu. M. Timofeyev, and A. V. Polyakov, J. Quant. Spectrosc. Radiat. Transfer **56** (5), 783 (1996).
2. V. I. Starikov and N. N. Lavrent'eva, *Collisional Broadening of Spectral Lines of Molecules of Atmospheric Gases* (IOA SB RAN, Tomsk, 2006) [in Russian].
3. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955; Inostrannaya Literatura, Moscow, 1959).
4. W. Gordy and R. L. Cool, *Molecular Spectra, Techniques of Chemistry* (Wiley, New York, 1984), Vol. **7**.
5. G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 1: *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1958; Inostrannaya Literatura, Moscow, 1949).
6. J. H. Van Vleck, Astrophys. J. **80** (3), 161 (1934).
7. R. M. Hill and W. Gordy, Phys. Rev. **93**, 1019 (1954).
8. L. G. Stafford and C. W. Tolbert, J. Geophys. Res. **68**, 3441 (1994).
9. E. E. Reber, J. Geophys. Res. **77**, 3831 (1972).
10. J. W. Waters, Nature **242**, 506 (1973).
11. H. J. Liebe, Int. J. Infrared Mill. Waves **10**, 631 (1989).
12. H. J. Liebe, P. W. Rosenkranz, and G. A. Huord, J. Quant. Spectrosc. Radiat. Transfer **48** (5/6), 629 (1992).
13. M. Yu. Tretyakov, M. A. Koshelev, V. V. Dorovskikh, et al., J. Mol. Spectrosc. **231**, 1 (2005).
14. E. W. Smith, J. Chem. Phys. **74** (12), 6658 (1981).
15. R. G. Gordon, Adv. Magn. Res. **3**, 1 (1968).
16. N. N. Filippov and M. V. Tonkov, J. Quant. Spectrosc. Radiat. Transfer **50** (1), 111 (1993).
17. P. W. Rosenkranz, IEEE Trans. Antenn. Propag. **23**, 498 (1975).
18. C. J. Tsao and B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer **2**, 111 (1961).
19. R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
20. H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
21. L. S. Rothman and A. Barbe, et al., J. Quant. Spectrosc. Radiat. Transfer **82** (1), 5 (2003).

Translated by V. Rogovoǐ

SPELL: OK