Analytical representation for the coefficients of pressure broadening of the ozone absorption lines by oxygen, air, and self-broadening

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Parameters of the analytical model for the coefficients of pressure broadening, γ, of the ozone absorption lines by oxygen, air, and self-broadening are determined. The model allows the calculation of γ to be done without the use of semiclassical methods in a broad range of rotational quantum numbers and temperatures being of interest in atmospheric studies.

Introduction

The study of vibrational-rotational (VR) spectra of ozone molecules has a long history because of the specific role of ozone in the atmosphere. The list of papers on the experimental and theoretical research of the ozone spectra includes more than a hundred publications. A review of bibliography on the broadening coefficients, γ, of the ozone lines can be found in Ref. 1.

The coefficients γ are extremely important in analyzing the vertical ozone distribution in the near-surface atmosphere. The knowledge of the broadening coefficients γ_{N_2} and γ_{O_2} by the main atmospheric gases, N_2 and O_2, virtually allows one to calculate the coefficient of broadening by air using the equation

$$\gamma_{air} = 0.79\gamma_{N_2} + 0.21\gamma_{O_2}. \quad (1)$$

The interest to the broadening coefficients for rotational ozone lines is caused by the fact that in the range of 10–100 cm^{-1} about 80 percent of emission lines of the upper atmosphere are the lines of $^{16}O_3$ and its isotopomers.[2]

Basic data on the broadening coefficients of rotational ozone lines (for the range from 50 to 90 cm^{-1}) for the case of air, oxygen, and self-broadening can be found in Ref. 2, where the values of γ are provided for 101 lines corresponding to $7 \le J \le 34$, $3 \le K_a \le 11$ and temperatures $T = 296$, 252 and 212 K.

The coefficients γ of broadening by air, nitrogen, oxygen, and self-broadening for the vibrational bands ν_2 and $\nu_1 + \nu_3$ and for the rotational band have been determined in Refs. 3 to 5. For the ν_2 band (630–800 cm^{-1}), the values of γ have been determined for 350 lines ($0 \le J \le 45$, $1 \le K_a \le 12$) at temperatures from +29°C down to –63°C. For the band $\nu_1 + \nu_3$, measurements were performed for 35 lines at $T = 227$ and 186 K. For the majority of lines studied in Refs. 2 to 5 the power n of the temperature dependence of γ was determined using the following relationship

$$\gamma(T) = \gamma(T_0)(T_0/T)^n, \quad (2)$$

where T_0 is the reference temperature (usually $T_0 = 296$ K). For this purpose, several spectra recorded at different temperatures were used simultaneously. The analysis of these spectra gave the averages for $\gamma_{av}(T_0)$ and n_{av}. In particular, for the rotational band, according to Ref. 2, $n_{av}(O_3 - O_3) = 0.67$, $n_{av}(O_3 - \text{air}) = 0.73$ and $n_{av}(O_3 - O_2) = 0.67$. For the band ν_2 $n_{av}(O_3 - \text{air}) = 0.53$ and for ν_1 $n_{av}(O_3 - \text{air}) = 0.67$.[3]

As shown in the overview (Ref. 1) the accuracy of determining the coefficients γ must be about 5%, but according to Ref. 2, the actual accuracy was about 10%.

Calculations of the broadening coefficients γ for ozone molecule done using semiclassical techniques are presented in the HITRAN database of spectroscopic information.[6] Though there is a lot of data available on the broadening coefficients γ of VR ozone lines, it is still insufficient because the demand for this data is much higher.

This study aims at determining the parameters of an analytical model for the coefficients of VR lines broadening in the ozone molecular absorption spectrum based on the experimental data available. This model has earlier been used (Refs. 7, 8) in describing the coefficients γ of water vapor molecule lines for the case of self-broadening and broadening by atoms of noble gases. The analytical model allows us to calculate the values of γ for a wide range of rotational quantum numbers and temperatures without the use of semiclassical calculation methods, for which it is essential to know the VR wave functions, energies, intermolecular potential, and other characteristics of the interacting molecules.

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1. Modeling the γ coefficients of broadening by oxygen, air, and self-broadening of ozone lines

Experimental values for the broadening coefficients γ for ozone molecule in the cases of broadening by these gases were used for determining the parameters of an analytical model that was used earlier[7,8] for modeling the coefficients γ in the systems H_2O-H_2O and H_2O-A (A stands for the noble gas atoms)

$$\gamma(K_i, K_f) = \gamma(sur) = x_1 + x_2\cosh[x_5(K_i - K_f)(K_i + K_f)]/ \\ /\{\cosh[x_3(K_i - x_4)]\cosh[x_3(K_f - x_4)]\}. \quad (3)$$

In this equation, $K_i \equiv K_a^i$ and $K_f \equiv K_a^f$ are the rotational quantum numbers of the initial and final states (the dependence on the quantum numbers K_c^i and K_c^f is neglected), and x_k refers to the parameters depending on the rotational quantum numbers J_i, J_f. The dependence of the parameters $x_k = x_k(J_i, J_f)$ is chosen to have the polynomial form

$$x_k = x_{k0} + x_{k1}(J_i + J_f) + x_{k2}(J_i + J_f)^2. \quad (4)$$

The parameters x_{k0}, x_{k1} and x_{k2} are determined by the least squares method by fitting Eqs. (3) and (4) to the known values of $\gamma_i(u)$ for the broadening coefficients. To characterize the fitting quality, as usual, we have chosen the following quantity

$$\sigma = \left\{\sum_i^N [\gamma_i(u) - \gamma_i(sur)]^2/(N - L)\right\}^{1/2}, \quad (5)$$

characterizing the root-mean-square deviation (N is the number of data used; L is the number of model parameters). Equation (3) determines a two-dimensional surface $\gamma(sur)$ at fixed rotational quantum numbers J_i and J_f. The sections of this surface determine the broadening coefficients γ for the spectral line $[J_i, K_a^i, K_c^i] \to [J_f, K_a^f, K_c^f]$.

Usually, the temperature dependence of the broadening coefficients γ is determined by Eq. (2), that is, the value n is specified for each line. In Refs. 7 and 8 the authors use a different approach to the description of the temperature dependence of broadening coefficients, namely, they use the dependence of γ on temperature that is determined through the temperature dependence of the surface $\gamma(sur)$, Eq. (3), by introducing the temperature dependence of the parameters that determine this surface. The dependence of the parameters, from Eq. (3), on temperature is introduced by analogy with Eq. (2)

$$x_k(T) = x_k(T_0)(T/T_0)^{n_k}, \quad (6)$$

where $x_k(T_0)$ is determined by the characteristics from Eq. (4) at the reference temperature $T_0 = 296$ K.

2. Determination of the analytical model parameters at $T_0 = 296$ K

We have obtained several sets of parameters for the analytical model $\gamma(sur)$ (3) that correspond to different sets of experimental data.

A. *Rotational transitions.* To determine the parameters of $\gamma(sur)$ (3) we used experimental data from Ref. 2, that is $\gamma(T_0 = 296\ \text{K})$ for 93 lines with the maximum values of $J_i = 35$ and $K_a^i = 12$ (for all the lines, $\Delta K_a = |K_a^i - K_a^f| = 1$). The model parameters for $\gamma(sur)$ are given in Table 1.

B. *Band* ν_2. For $\gamma_i(u)$ in Eq. (5) we used the experimental data $\gamma(T_0 = 296\ \text{K})$ from Ref. 3. The parameters of the model for this band are also given in Table 1.

The quality of the experimental data reconstruction for the two bands can be judged based on data presented in Table 2, which summarizes the statistics of calculating the coefficients γ using the model $\gamma(sur)$ (3). As is seen from Table 2 about 90% of the data on γ obtained for the rotational band are retrieved

Table 1. The parameters $x_{km}(T_0 = 296\ \text{K})$ from Eqs. (3) and (4) for the broadening coefficients of VR transitions of ozone for the cases of broadening by air, oxygen, and self-broadening

Parameter	$O_3 - O_3$		$O_3 -$ air		$O_3 - O_2$
	Rotational band	Band ν_2	Rotational band	Band ν_2	Rotational band
x_{10}		0.0816 ± 0.002	0.0709 ± 0.009	0.0818 ± 0.0093	0.0717 ± 0.007
x_{20}	0.1084 ± 0.0017	0.0290 ± 0.002	0.0212 ± 0.0260	0.0117 ± 0.0012	0.0154 ± 0.029
x_{21}	$-(0.1964 \pm 0.029)\cdot 10^{-3}$	$-(0.2117 \pm 0.021)\cdot 10^{-3}$	$-(0.389 \pm 0.078)\cdot 10^{-3}$	$-(0.4061 \pm 0.021)\cdot 10^{-3}$	$-(0.444 \pm 0.051)\cdot 10^{-3}$
x_{30}	0.0381 ± 0.017	0.1774 ± 0.024	0.1992 ± 0.0094	0.0623 ± 0.0094	0.2182 ± 0.024
x_{31}					
x_{40}		2.2925 ± 0.22			
x_{41}			0.2511 ± 0.0176	-0.1183 ± 0.0085	0.1366 ± 0.0085
N	93	369	93	345	93
L	3	5	5	5	5
ΔK_a	1	1	1	1	1
σ	$3.0\cdot 10^{-4}$	$2.8\cdot 10^{-4}$	$2.9\cdot 10^{-4}$	$1.4\cdot 10^{-4}$	$2.4\cdot 10^{-4}$

Note. The parameters were obtained for the lines having $\Delta K_a = 1$ and can be used in the calculations of only these lines. The parameters x_{10}, x_{20}, and x_{21} have dimensions $\text{cm}^{-1}\cdot\text{atm}^{-1}$, other parameters are dimensionless.

Table 2. Statistics of the calculations of the γ coefficients for VR transitions of ozone at $T_0 = 296$ K

Δ, %	$O_3 - O_3$				$O_3 -$ air				$O_3 - O_2$	
	Rotational band		Band ν_2		Rotational band		Band ν_2		Rotational band	
	N_L	N_L/N, %	N_L	N_L/N, %	N_L	N_L/N, %	N_L	N_L/N, %	N_L	N_L/N, %
0–5	84	90.3	252	68.3	82	88.2	305	88.7	83	89.2
5–10	8	8.6	85	23.6	9	9.7	35	10.1	8	8.6
10–20	1	1.1	31	8.4	2	2.1	4	1.2	2	2.2
> 20	0	0	1	0.3	0	0	0	0	0	0

Note. $\Delta = |\gamma(\text{exp.}) - \gamma(sur)|/\gamma(\text{exp.})$, N_L is the number of lines for which this variance Δ was obtained.

Table 3. The parameters $x_{km}(T_0 = 296$ K) and n from Eqs. (3), (4), (6) determining the temperature dependence of the broadening coefficients of VR transitions of ozone for the cases of broadening by air, oxygen, and self-broadening

Parameter	$O_3 - O_3$	$O_3 -$ air	$O_3 - O_2$
x_{20}	0.1098 ± 0.0007	$(0.9178 \pm 0.0023) \cdot 10^{-1}$	$(0.8303 \pm 0.0072) \cdot 10^{-1}$
x_{21}	$-(0.1998 \pm 0.0176) \cdot 10^{-3}$	$-(0.2788 \pm 0.0045) \cdot 10^{-3}$	$-(0.3311 \pm 0.0166) \cdot 10^{-3}$
x_{30}	$-(0.4320 \pm 0.0183) \cdot 10^{-1}$	$(0.6528 \pm 0.0178) \cdot 10^{-1}$	$(0.8456 \pm 0.0623) \cdot 10^{-1}$
x_{31}	$(0.6784 \pm 0.4796) \cdot 10^{-4}$	$-(0.831 \pm 0.033) \cdot 10^{-3}$	$-(0.1267 \pm 0.0145) \cdot 10^{-2}$
x_{41}	0.0	0.2258 ± 0.0061	0.2480 ± 0.0066
n_2	-0.6474 ± 0.0157	-0.5409 ± 0.0067	-0.6864 ± 0.0121
n_4	0.00	0.5411 ± 0.1110	0.0
N	648	1140	385
L	6	7	7
ΔK_a	≤ 1	≤ 1	≤ 1
σ	$1.8 \cdot 10^{-4}$	$7.6 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$

accurate to 5% and, in fact, all data are retrieved accurate to 10%, which corresponds to the experimental accuracy of determining these parameters. To reconstruct γ, we need no more than five parameters, and for the case of self-broadening, this number is reduced to three. This points to the fact that the model $\gamma(sur)$ (3) adequately describes the experimental data on the rotational band. Similar results were obtained for the band ν_2. Somewhat worse is the quality of reconstruction in the case of self-broadening. However even in this case about 92% of the experimental data on γ are reconstructed accurate to about 10%.

3. Determination of the temperature dependence

The temperature dependence $\gamma(sur)$ (3) was determined by Eqs. (4) and (6) with the following data used as input values for $\gamma_i(u)$ in Eq. (5).

System O_3–O_2. For this system, we used the values for $\gamma(T_0 = 296$ K) and temperature-dependence power n for 93 rotational lines from Ref. 2. Equation (2) was used to calculate the values of γ at the temperatures $T = 252$ and 212 K, that is, for the temperatures at which the absorption spectra were recorded. This data were completed with the values of $\gamma(T)$ determined in Ref. 4 for 35 lines of the band $\nu_1 + \nu_3$ at $T = 227$ and 186 K. The resulting set of the coefficients $\gamma(T)$ at different T was used to determine the parameters of the model $\gamma(sur)$ (3). These parameters are given in Table 3.

Note that to describe the temperature dependence we used only one parameter n_2 (other parameters cannot be statistically determined). The quality of reconstructed data is shown in Figs. 1 and 2. All the data have been structurized from the viewpoint of the growth of experimental values of the broadening coefficients marked by dark (filled) symbols. Blank symbols correspond to the calculated values of the coefficients γ. Figures 1 and 2 demonstrate high quality of the γ reconstruction especially for the band $\nu_1 + \nu_3$.

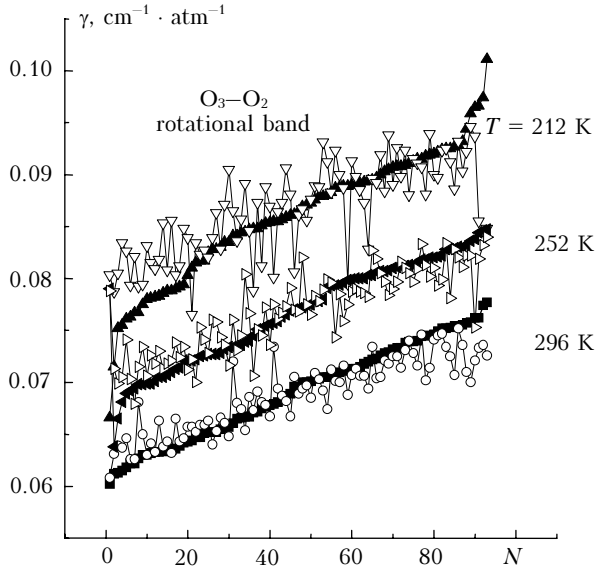

Fig. 1. Experimental (Ref. 2) and calculated by the analytical model $\gamma(sur)$ (3) broadening coefficients of VR lines of the rotational band of ozone molecule at different temperatures for the case of broadening by oxygen (parameters of Table 3 were applied).

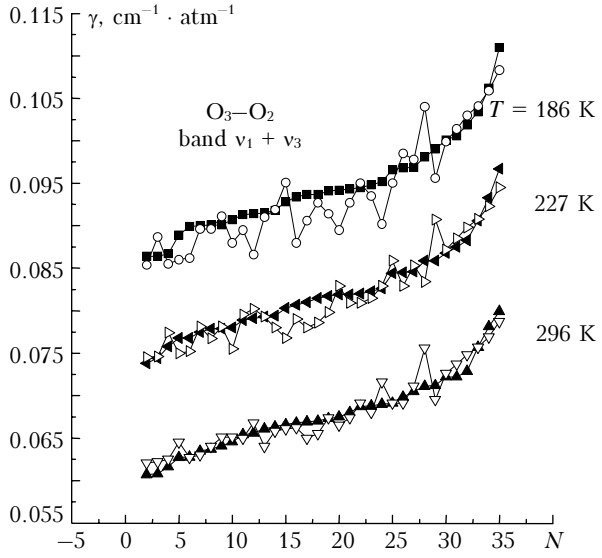

Fig. 2. Experimental (Ref. 4) and calculated by the analytical model $\gamma(sur)$ (3) broadening coefficients of VR lines of the band $\nu_1 + \nu_3$ of ozone molecule for the case of broadening by oxygen.

System O_3–O_3. For this system, we used the values of $\gamma(T_0 = 296\ \text{K})$ for the rotational band (Ref. 2) and for the band ν_2 (Ref. 3). Using the temperature-dependence power n, for 93 rotational lines, using Eq. (2) we found the values of $\gamma(T)$ at $T = 252$ and 212 K. From the set of $\gamma_i(u)$ values obtained we determined the parameters of the model $\gamma(sur)$ (3), summarized in Table 3, and the quality of reconstruction of broadening coefficients is shown in Fig. 3. With the exception of some lines, the coefficients γ have been reconstructed accurate to 10%.

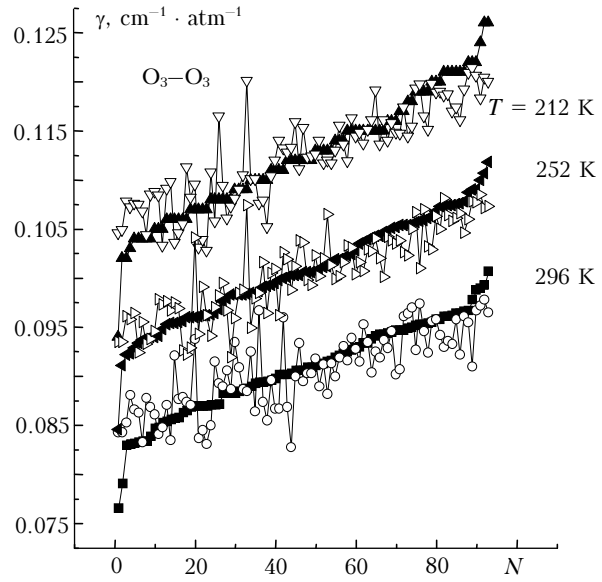

Fig. 3. Experimental (Ref. 2) and calculated by the analytical model $\gamma(sur)$ (3) broadening coefficients of VR lines of the rotational band of ozone molecule for the case of self-pressure broadening.

System O_3 – air. Using the values of $\gamma(T_0 = 296\ \text{K})$ and n (Ref. 2) we determined the values of $\gamma(T)$ for $T = 252$ and 212 K for rotational transitions and using the values of $\gamma(T_0 = 296\ \text{K})$ and n (Ref. 3) we also determined the values of $\gamma(T)$ at $T = 250$ and 210 K for the band ν_2. We completed them with the values of $\gamma(T)$ at $T = 227$ and 186 K calculated by Eq. (1) using $\gamma(T_0 = 296\ \text{K})$ and n (Ref. 4) for the systems O_3–N_2 and O_3–O_2 for the band $\nu_1 + \nu_3$. Analysis of the model results $\gamma(sur)$ (3) fitted to these values shows that these values are incompatible in the sense that the data for the rotational band at $T = 212$ K are poorly described if combined with the data at $T = 210$ K for the band ν_2. It is mentioned in the introduction that the average value of temperature-dependence power $n_{av}(O_3 - \text{air})$ equals 0.73 for the rotational transitions, and $n_{av}(O_3 - \text{air})$ equals 0.53 for the band ν_2, i.e., there is a difference. In the final variant, the data on the bands ν_2 and $\nu_1 + \nu_3$ was used. The obtained parameters of the model $\gamma(sur)$ (3) are given in Table 3.

The quality of reconstruction of the data used is shown in Figs. 4 and 5 and seems to be quite satisfactory.

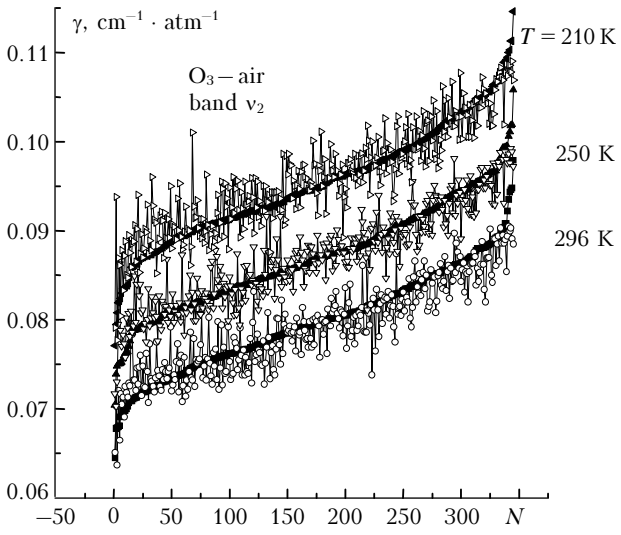

Fig. 4. Experimental (Ref. 3) and calculated by the analytical model $\gamma(sur)$ (3) broadening coefficients of VR lines of the band ν_2 of ozone molecule for the case of broadening by air.

4. Discussion

The main results of work done are summarized in Tables 1 and 3. The parameters of the analytical model $\gamma(sur)$ (3) given in them allow us to calculate the broadening coefficients γ of VR ozone absorption lines for cases of oxygen, air, and self-pressure broadening for the rotational quantum numbers $J \le 45$, $K_a \le 12$ and temperatures of +29°C down to −63°C. The practice of using the model $\gamma(sur)$ for water vapor (Refs. 7, 8) shows that the model

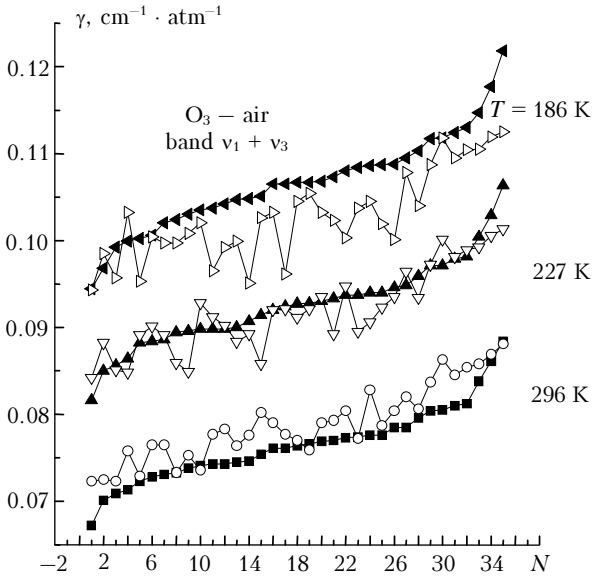

Fig. 5. Experimental (Ref. 4) and calculated by the analytical model γ(*sur*) (3) broadening coefficients of VR lines of the band $\nu_1 + \nu_3$ of ozone molecule for the case of broadening by air.

parameters can be used for the calculation of γ for a larger range of rotational quantum numbers and temperatures. The restrictions on the model applications concern the limitations on $\Delta K_a = |K_a^i - K_a^f| = 0$; 1 (only for these transitions in the inverse problem the experimental values for the coefficients γ were used, so the parameter x_5 in the model remained undetermined). The experimental data reconstruction accuracy, as seen from Table 2 and Figs. 1–5, is about 10% for more than 90% of data and which is quite satisfactory. The largest errors occur for the lines with the least and the largest values of the quantum number $K_a = 0$ or $K_a = J$.

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