

SHIFTS OF THE ABSORPTION LINE CENTERS FROM THE OZONE VIBRATIONAL BANDS $\nu_1 + \nu_3$, $2\nu_1$ AND $2\nu_3$ CAUSED BY N_2 AND O_2 PRESSURE

A. Barbe, S. Bouazza, J.J. Plateaux, A.D. Bykov, N.N. Lavrent'eva, and L.N. Sinitsa

*G.S.M.A. Reims University, France
Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
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Measurement data on line shift coefficients of $\nu_1 + \nu_3$, $2\nu_1$ and $2\nu_3$ absorption bands of ozone in the case of N_2 and O_2 foreign gases are discussed. The measurements have been carried out using a Fourier spectrometer of Reims University and a White-type absorption cell with an optical length of 816 cm. Spectral resolution was 0.002 cm^{-1} , and the accuracy of the shift coefficient measurements was about $0.001 \text{ cm}^{-1}\cdot\text{atm}^{-1}$. Calculations have been done using the Anderson method. Components of the ozone molecule polarizability tensor for the vibrational states (101), (200), and (002) were determined by the least-squares fitting using data on shifts of some lines of a band.

Temperature dependence of the shift coefficients has also been studied. Good agreement between the experimental and calculational data demonstrates usefulness of the Anderson technique for calculations of line shifts in the absorption spectrum of ozone molecules.

INTRODUCTION

At present the positions, intensities, and broadening coefficients for absorption lines of the ozone and its isotopic modifications have been measured with high accuracy in a wide spectral range from 600 to 3700 cm^{-1} (see Refs. 1–5). Theoretical analysis of the experimental data including the line assignment, determination of rotational, centrifugal distortion constants, parameters of the dipole moments of transition, and calculations of coefficients of line broadening caused by N_2 and O_2 pressure has essentially widened and improved our knowledge of the ozone spectroscopic properties.

Several recent studies^{6–9} concerned the investigation of line shift coefficients of the ozone molecule. Measurements of the shift for four lines of ν_3 band and for sixty four lines of ν_1 band caused by N_2 and O_2 pressure are presented in Ref. 6. The shift coefficients for about one hundred fifty lines of $\nu_1 + \nu_3$ band were measured in Refs. 7 and 8. Calculations of the shift coefficients and comparison with the experimental data for $\nu_1 + \nu_3$ band have been carried out in Ref. 9.

In this paper we present the measurements and calculations done by the Anderson–Tsao–Curnutte (ATC) method for the line shifts for three vibrational bands of $\nu_1 + \nu_3$, $2\nu_1$, and $2\nu_3$ caused by oxygen and nitrogen pressure.

EXPERIMENT

The spectra were recorded using a Fourier spectrometer of the Reims University. The spectrometer and measurement technique have been described in Ref. 10. We used an InSb detector, a CaF_2 beamsplitter, and a globar as a light source.

The measurements of line shifts for $\nu_1 + \nu_3$ band were described earlier in Refs. 7 and 8. Since $2\nu_1$ and $2\nu_3$ vibrational bands are weaker than the $\nu_1 + \nu_3$ band the technique used to measure line shifts in $\nu_1 + \nu_3$ band (see Refs. 7 and 8) was modified. The measurements for the lines of $2\nu_1$ and $2\nu_3$ bands were carried out using a White cell with optical path length of 816 cm at ozone pressure from 1 to 10 Torr, and the buffer gas pressure varied from 80 to 300 Torr. As in Ref. 7, we used another cell 3 cm in length, as an etalon. Lines of the ν_3 band of N_2O are used as reference lines. This allowed us to eliminate small frequency shifts observed when recording different spectra.

The data processing included the least-squares fitting of Voigt profile. The values of thus measured shift coefficients are given in tables. Since raw experimental data were obtained from observations of different spectra the data presented in the tables are mean values of the measured quantities.

It is difficult to determine actual measurement accuracy of these data because it may depend on many factors as, for example, the contributions that may come from other lines. Moreover the use of White's cell worsens the signal-to-noise ratio compared with the measurements in $\nu_1 + \nu_3$ band. In this case the signal-to-noise ratio was equal to 800 (see Refs. 7 and 9). The final estimation of the accuracy yielded the $10^{-3} \text{ cm}^{-1}\cdot\text{atm}^{-1}$ value for it.

CALCULATIONS OF SHIFT COEFFICIENTS

To make calculations we used a simple version of a semiclassical theory of collisional broadening of spectral lines in the form of the Anderson–Tsao–Curnutte (ATC) method.^{11,12}

The calculations carried out in Refs. 13–15 confirmed the idea that the ATC method gives quite accurate results for polar molecules. In Refs. 16 and 17 it has been shown that it allows quite accurate calculations of the H₂O absorption line shifts due to collisions with nitrogen and oxygen molecules to be done.

Within the framework of the ATC method the half-width γ_{if} of a line and the line center shift δ_{if} are defined according to the relation^{11–14}:

$$\gamma_{if} - i \delta_{if} = \frac{n}{c} \sum_{j_2} \rho_{j_2} \int_0^{\infty} dv v f(v) \int_0^{\infty} db b S(b), \quad (1)$$

where i and f are quantum numbers of the initial and final states of a molecule involved in the transition, j_2 denotes quantum numbers of states of a foreign gas molecule (i , f , and j_2 include the vibrational and rotational quantum numbers), n is the number density of the foreign gas, v is the relative velocity of colliding molecules, $f(v)$ is the Maxwell distribution function, ρ_{j_2} is the population of j_2 level of a broadening molecule, and b is the impact parameter. The collision efficiency function is presented in the following form:

$$S(b) = 1 - \sum_{j_2} \sum_{M, M'} \frac{\langle j_f(M_f) p(M) | j_i(M_i) \rangle \langle j_f(M_f) p(M) | j_i(M_i) \rangle}{(2j_i + 1)(2j_2 + 1)} \times \\ \times \langle f j_2 | T^{-1}(b) | f j_2 \rangle \langle i j_2 | T(b) | i j_2 \rangle, \quad (2)$$

where $\langle j_i(m_1) j_2(m_2) | j(m) \rangle$ are the Clebsch–Gordan coefficients, T is the time evolution operator, $p = 1$ is dipole radiation, $p = 2$ is quadrupole radiation, etc. The summation is carried out over all magnetic quantum numbers. The states i and i' differ only by the projections of the angular momentum M_i and $M_{i'}$ onto the Z axis of coordinate system. The same holds for f and f' states. According to the ATC method

$$S(b) = S_1(b) + S_2(b) + \dots \quad (3)$$

Here $S_1(b)$ as the first-order term of a series over intermolecular potential determines the vibrational phase shift. The second-order term $S_2(b)$ for O₃–N₂, O₂ can be represented in the following form:

$$S_2(b) = {}^{12}S_2^e(b) + {}^{22}S_2^e(b) + {}^{22}S_2^p(b) + {}^{02}S_2^p(b) + {}^{20}S_2^p(b), \quad (4)$$

where the superscripts denote multipolarity of the interactions. The terms marked with superscript e denote the electrostatic part of the potential and terms marked with superscript p denote its polarization part. The term ${}^{12}S_2^e(b)$ describes the contribution coming from the dipole–quadrupole interaction potential. The terms ${}^{22}S_2^p(b)$, ${}^{02}S_2^p(b)$, and ${}^{20}S_2^p(b)$ describe the contributions coming from the polarization and dispersion potentials. The terms corresponding to dipole–dipole and quadrupole–dipole interactions are omitted here since the collisions with N₂

and O₂ nonpolar molecules will be considered later. Formulas for the terms of Eq. (4) can be found in Refs. 12 and 18.

Let us note that only isotropic part of the potential contributes to $S_1(b)$ and its contribution is determined by $(d_i - d_f)$ and $(\alpha_i - \alpha_f)$ differences. Contributions coming from ${}^{22}S_2^p(b)$, ${}^{02}S_2^p(b)$, and ${}^{20}S_2^p(b)$ depend on $(\alpha_i - \alpha_i^{zz})$, $(\alpha_f - \alpha_f^{zz})$, $(\alpha_i^{xx} - \alpha_i^{yy})$, and $(\alpha_f^{xx} - \alpha_f^{yy})$ values. Here d_i and d_f are the dipole moments of the initial and final states, α_i , α_f are corresponding mean polarizabilities and α_i^{zz} , α_i^{xx} , α_i^{yy} , α_f^{zz} , α_f^{xx} , α_f^{yy} are components of the polarizability tensors of the absorbing molecule in the initial and final states, respectively.

In Ref. 16 it has been shown that the vibrational dependence of the line shift coefficients of water vapor is explained by the intermolecular potential. In this case the shift is mainly determined by the contributions from the electrostatic potential (${}^{12}S_2^e(b)$ in Eq. (4)) and from the polarization one ($S_1(b)$). In contrast to water vapor molecule, ozone has a three times smaller (0.53 D) dipole moment while a two times greater polarizability (2.8 Å³).

Therefore it is expected that in the case of O₃–N₂ or O₃–O₂ collisions the contribution coming from the polarization part of the intermolecular potential in the second order of interruption function of O₃ is larger, that is, the contributions ${}^{22}S_2^p(b)$, ${}^{02}S_2^p(b)$, and ${}^{20}S_2^p(b)$ must be significant in value. For this reason the calculations took into account not only the electrostatic terms corresponding to dipole and quadrupole interactions but also the terms describing the interactions like dipole–induced dipole. Contributions from the polarization potential to $S_2(b)$ have been estimated by formulas from Ref. 18, and resonance functions Ig₁ and Ig₂ were determined earlier in Ref. 19.

The parameters used in calculations are presented in Table I. The calculations have been carried out for the temperature 297 K. Dependence of the mean dipole moment on the vibrational states was neglected since the corresponding contributions were found to be too small. For this same reason we neglected the influence of intramolecular interactions on i – i' and f – f' dipole transitions. To calculate the energy levels and wave functions the Watson effective Hamiltonian was used (without account for Coriolis and Darling–Dennison resonances). From direct calculations it was found that the neglect of accidental resonances does not result in significant errors in the calculations of the line half-widths and line shifts.

The rotational and centrifugal distortion constants of the ground and excited vibrational states were taken from Refs. 1 and 20.

Determination of components of the polarizability tensor of the ozone molecule responsible for induction and dispersion interactions was the most difficult problem in this study. The components of the polarizability tensor for the ground vibrational states have been measured in Ref. 21 and calculated in Ref. 22, the first derivatives of the polarizability with respect to the normal coordinates were also determined, but we need the second derivatives for estimating the polarizability in the excited states. For this reason α_f and α_f^{zz} parameters (polarizability of the upper vibrational state and zz –component of the polarizability tensor) were determined using the least-squares method of fitting to the measured line shifts caused by nitrogen pressure for several lines. Since the difference between xx –

and yy -components of the polarizability tensor of the ozone molecule is small ($\alpha_f^{xx} - \alpha_f^{yy}$) was taken equal to this value in the ground vibrational state. Further the parameters defined by the fitting technique were used to calculate line shifts by oxygen pressure. It should be noted here that thus obtained parameters seem to be reasonable. Since the mean polarizabilities of excited states exceed the polarizability in the ground state only by about 10% a good agreement with the estimations by the theory of vibrational-rotational spectra can be stated.

TABLE I. Molecular and spectroscopic constants used in calculations.

Parameter	Value		
	O ₃	N ₂	O ₂
Dipole moment, D	-0.532	—	—
Quadrupole moment, DÅ	θ_{xx} -1.4	1.4	0.4
	θ_{yy} -0.7		
	θ_{zz} 2.1		
Ionization potential, 10 ⁻¹¹ erg	2.126	2.486	2.003
Polarizability, Å ³	α_i 2.8	1.76	1.59
	α_i^{xx} 2.0		
	α_i^{yy} 1.8		
	α_i^{zz} 4.6		
	α_f 2.890	(101)	
	α_f^{zz} 5.142	(101)	
	α_f 2.845	(200)	
	α_f^{zz} 5.004	(200)	
	α_f 2.875	(002)	
	α_f^{zz} 4.680	(002)	
Rotational constant, cm ⁻¹	Refs. 1 and 18	1.998	1.4456
Statistical weight of even levels of odd levels	1	2	1
	0	1	0

DATA ANALYSIS

The calculated and measured line shift coefficients for three vibrational bands of the ozone molecule (J'' varies from 2 to 43) are presented in Tables II–V. In the first and second columns of the tables the quantum numbers of upper and lower rotational levels are presented. The contributions from different terms of $S_2(b)$ function into the shift, the contribution from $S_1(b)$, the whole line shift, and its measured value are given in this order in the next columns. The fifth column of the tables shows the summed contribution of the last three terms of Eq. (4).

The measured line shifts of $2\nu_1$ and $2\nu_3$ bands show that on the whole the shift coefficients in the first band are smaller while in the second one they are larger than for $\nu_1 + \nu_3$ band. The greatest measured value of the shift coefficient in $2\nu_1$ band is -3.4 mK/atm while the

smallest shift coefficient in $2\nu_3$ band is about -4.8 mK/atm. One can easily see the dependence of shift on the rotational quantum number J' . The shift increases with its growth. This confirms the conclusions drawn in Ref. 7 from analysis of $\nu_1 + \nu_3$ band. Thus a strong vibrational effect in the shift coefficients for ozone absorption lines and its dependence on rotational quantum number should be noted.

Comparison of the calculational results with experimental data shows a good agreement between them. The standard deviation is $1.2 \cdot 10^{-4}$ cm⁻¹·atm⁻¹, statistics of the $\Delta = |\delta_{\text{exp}} - \delta_{\text{calc}}|$ deviations is the following.

$\Delta \leq 0.0005$	51% of all lines
$0.0005 < \Delta \leq 0.0010$	34.9%
$0.0010 < \Delta \leq 0.0015$	9.3%
$0.0015 < \Delta \leq 0.0020$	2.3%
$0.0020 < \Delta$	2.3%

The difference between the calculated and measured data does not exceed 0.001 cm⁻¹·atm⁻¹ for more than 80% lines.

From the data presented in Tables II–V it follows that electrostatic interactions give small contributions to the ozone line shift. The line shift is mainly caused by induction and dispersion interactions. For all three bands the contributions coming from these interactions to $S_2(b)$ is positive but it is negative in the case of $S_1(b)$. Thus some compensation for contributions occurs.

Table III presents the line shift coefficients for lines of the $\nu_1 + \nu_3$ band caused by oxygen pressure. The calculations are in a good agreement with measurements. As it has already been noted the α_f and α_f^{zz} parameters determined for O₃–N₂ line shifts were then used in calculations, of O₃–N₂ shifts and the data presented in Table III can be considered only as a prediction. Good agreement in this case confirms the correctness of the calculational technique. The statistics of line shifts deviations for the case of O₃–O₂ collisions is the following.

$\Delta \leq 0.0005$	58.1% of all lines
$0.0005 < \Delta \leq 0.0010$	30.2%
$0.0010 < \Delta \leq 0.0015$	7.1%
$0.0015 < \Delta \leq 0.0020$	0.0%
$0.0020 < \Delta$	4.6%

The line shifts by collisions with oxygen molecules are larger due to an increasing contribution from $S_1(b)$ with decreasing impact parameter b_0 and the corresponding decrease of the broadening coefficients. Moreover, the contribution coming from the polarization potential $S_2(b)$ has a positive sign, as in the case of the line shifts caused by nitrogen pressure.

In contrast to polarization of water vapor molecules the interactions in the ozone are noticeable already in transitions to low vibrational states, what is caused by strong polarizability of the ozone molecule.

TABLE II. Coefficients of the O₃ line shifts (mK/atm) caused by N₂ pressure for $\nu_1 + \nu_3$ band.

J'	K'_a	K'_c	J''	K''_a	K''_c	S_2			S_1	Shift		n
						dq	qq	pol		Calc.	Exper.	
42	2	41	43	2	42	0.002	0.006	0.831	-4.122	-3.28	-4.2	0.78
38	5	34	39	5	35	-0.003	-0.010	1.914	-5.149	-3.25	-4.0	0.94
37	4	33	38	4	34	-0.034	-0.005	2.799	-5.430	-2.60	-4.0	1.10
34	6	29	35	6	30	-0.020	0.004	2.377	-5.737	-3.37	-3.6	1.10
32	5	28	33	5	29	0.002	-0.004	2.486	-5.404	-2.92	-2.8	1.06
31	6	25	32	6	26	-0.018	0	2.503	-5.755	-3.27	-2.4	1.10
31	5	26	32	5	27	0.016	0.002	2.749	-5.574	-2.80	-2.6	1.12
31	1	30	32	1	31	0.006	0.010	1.196	-4.070	-2.85	-3.8	0.83
30	5	26	31	5	27	0.008	-0.002	2.566	-5.443	-2.86	-3.3	1.09
31	0	31	32	0	32	0.006	0.004	0.370	-3.908	-3.52	-4.4	0.74
30	1	30	31	1	31	0.005	0.004	0.424	-3.942	-3.50	-4.1	0.74
28	6	23	29	6	24	-0.014	0	2.619	-5.742	-3.14	-3.3	1.10
29	0	29	30	0	30	0.008	0.006	0.406	-3.903	-3.48	-3.2	0.75
27	6	21	28	6	22	-0.011	-0.001	2.633	-5.728	-3.11	-2.0	1.10
28	2	27	29	2	28	-0.001	0.004	1.298	-4.191	-2.89	-3.5	0.88
28	1	28	29	1	29	0.006	0.005	0.475	-3.946	-3.46	-3.1	0.76
27	1	26	28	1	27	-0.005	0.006	1.379	-4.040	-2.66	-3.7	0.87
27	0	27	28	0	28	0.008	0.009	0.448	-3.894	-3.43	-3.3	0.75
25	5	20	26	5	21	-0.015	0.005	2.589	-5.460	-2.88	-3.0	1.15
25	3	22	26	3	23	-0.009	-0.005	2.779	-4.956	-2.17	-2.9	1.08
24	6	19	25	6	20	-0.006	0.004	2.644	-5.647	-3.01	-2.2	1.10
25	1	24	26	1	25	-0.011	0.001	1.455	-4.028	-2.58	-2.4	0.90
24	5	20	25	5	21	-0.016	0.005	2.653	-5.439	-2.80	-3.0	1.13
24	4	21	25	4	22	-0.006	-0.006	2.371	-4.982	-2.62	-2.8	1.05
23	6	17	24	6	18	-0.005	0.004	2.628	-5.604	-2.98	-2.4	1.11
22	8	15	23	8	16	-0.001	-0.009	2.325	-5.555	-3.24	-3.2	1.04
23	5	18	24	5	19	-0.013	0.004	2.645	-5.417	-2.78	-2.8	1.13
22	7	16	23	7	17	-0.002	-0.002	2.441	-5.574	-3.14	-2.8	1.07
23	4	19	24	4	20	-0.001	0.003	2.787	-5.174	-2.38	-2.9	1.13
22	5	18	23	5	19	-0.012	0.004	2.675	-5.393	-2.73	-3.2	1.12
21	7	14	22	7	15	-0.002	-0.002	2.389	-5.487	-3.10	-2.5	1.06
35	20	15	35	20	16	-0.005	0.002	2.161	-6.296	-4.14	-2.8	0.98
23	0	23	24	0	24	0.012	0.011	0.550	-3.847	-3.27	-3.1	0.79
20	8	13	21	8	14	-0.001	-0.008	2.221	-5.356	-3.14	-1.5	1.02
20	7	14	21	7	15	-0.001	-0.001	2.331	-5.392	-3.06	-2.8	1.05
19	7	12	20	7	13	0	-0.001	2.272	-5.294	-3.02	-2.4	1.04
14	3	12	15	3	13	-0.019	-0.005	2.161	-4.382	-2.25	-2.1	1.01
10	4	7	11	4	8	-0.007	0.015	2.093	-4.379	-2.28	-1.8	0.99
8	4	5	9	4	6	-0.005	-0.014	1.888	-4.148	-2.25	-1.6	0.94
3	2	1	2	2	0	0.002	0.023	0.906	-3.322	-2.39	-0.6	0.81
27	0	27	26	0	26	0.008	0.009	0.448	-3.894	-3.43	-3.6	0.75
37	6	31	36	6	30	0.006	0.003	2.505	-5.772	-3.26	-2.6	1.09
37	2	35	36	2	34	0.012	0.003	1.789	-4.540	-2.74	-3.2	1.03

Note: 1 mK = 0.001 cm⁻¹.

TABLE III. Coefficients of the O_3 line shifts (mK/atm) caused by O_2 pressure for $\nu_1 + \nu_3$ band.

J'	K'_a	K'_c	J''	K''_a	K''_c	S_2			S_1	Shift	
						dq	qq	pol		Calc.	Exper.
42	2	41	43	2	42	0	0	0.93	-5.48	-4.54	-5.3
38	5	34	39	5	35	-0.001	-0.001	2.61	-7.30	-4.69	-4.8
37	4	33	38	4	34	0.004	0	4.23	-7.96	-3.73	-4.4
34	6	29	35	6	30	-0.002	0	3.95	-8.66	-4.71	-4.9
32	5	28	33	5	29	0	-0.001	3.61	-7.83	-4.22	-4.3
31	6	25	32	6	26	-0.002	0	4.15	-8.68	-4.53	-4.3
31	5	26	32	5	27	0.001	0	4.24	-8.24	-3.99	-3.7
31	1	30	32	1	31	0	0.001	1.34	-5.41	-4.06	-4.5
30	5	26	31	5	27	0	0	3.75	-7.91	-4.15	-4.3
31	0	31	32	0	32	0.001	0	0.41	-5.18	-4.76	-4.7
30	1	30	31	1	31	0	0	0.48	-5.24	-4.76	-4.5
28	6	23	29	6	24	-0.002	-0.001	4.26	-8.63	-4.37	-3.9
29	0	29	30	0	30	0.001	0.001	0.45	-5.17	-4.72	-4.7
27	6	21	28	6	22	-0.001	-0.002	4.25	-8.57	-4.33	-3.8
28	2	27	29	2	28	0	0	1.49	-5.61	-4.12	-4.2
28	1	28	29	1	29	0.001	0.001	0.53	-5.25	-4.71	-4.2
27	1	26	28	1	27	-0.001	-0.001	1.56	-5.38	-3.82	-4.0
27	0	27	28	0	28	0.001	0.001	0.50	-5.17	-4.66	-3.8
25	5	20	26	5	21	-0.002	0	3.80	-7.93	-4.13	-3.4
25	3	22	26	3	23	0	0	3.72	-6.99	-3.26	-3.5
24	6	19	25	6	20	-0.001	-0.001	4.05	-8.32	-4.27	-3.3
25	1	24	26	1	25	-0.001	0	1.66	-5.37	-3.72	-4.0
24	5	20	25	5	21	-0.002	0	3.85	-7.88	-4.03	-3.5
24	4	21	25	4	22	0	0	3.12	-6.98	-3.87	-4.0
23	6	17	24	6	18	-0.001	-0.001	3.93	-8.19	-4.26	-3.5
22	8	15	23	8	16	-0.001	-0.001	3.27	-7.94	-4.68	-3.3
23	5	18	24	5	19	-0.002	0	3.83	-7.84	-4.01	-3.6
22	7	16	23	7	17	0	-0.001	3.53	-8.05	-4.52	-3.6
23	4	19	24	4	20	0.001	0.001	3.81	-7.35	-3.53	-3.4
22	5	18	23	5	19	-0.002	0	3.82	-7.77	-3.95	-3.9
21	7	14	22	7	15	0	-0.001	3.38	-7.86	-4.49	-3.4
23	0	23	24	0	24	0.001	0.001	0.62	-5.12	-4.49	-4.0
20	8	13	21	8	14	-0.001	-0.002	2.98	-7.54	-4.56	-3.4
20	7	14	21	7	15	0	-0.001	3.22	-7.67	-4.45	-3.4
19	7	12	20	7	13	0	-0.002	3.07	-7.47	-4.41	-3.5
14	3	12	15	3	13	-0.002	0	2.57	-5.93	-3.37	-2.6
10	4	7	11	4	8	-0.001	0.002	2.45	-5.90	-3.45	-2.4
8	4	5	9	4	6	0	0.002	2.14	-5.52	-3.39	-2.5
3	2	1	2	2	0	0	0.003	0.96	-4.32	-3.36	-1.2
27	0	27	28	0	29	0.001	0.001	0.50	-5.17	-4.66	-3.8
37	6	31	36	6	30	0.001	-0.003	4.25	-8.77	-4.53	-3.3
37	2	35	36	2	34	0.002	-0.002	2.20	-6.20	-4.01	-3.9

TEMPERATURE DEPENDENCE OF THE SHIFTS

The last column of Table II presents the values of the exponent of temperature dependence of the ozone line shifts caused by N_2 pressure determined by the formula

$$\delta(t) = \delta(297) (297/T)^n. \quad (5)$$

Here $\delta(T)$ is the shift coefficient at temperature T . The calculations of line shift have been carried out for four temperatures (200, 230, 260, and 297 K), the temperature dependence exponents were determined by the least-squares method. The values of n for lines from the $\nu_1 + \nu_3$ band are presented in Table II.

It was revealed that simple formula (5) satisfactorily describes the temperature dependence. Standard deviation did not exceed $10^{-6} \text{ cm}^{-1} \cdot \text{atm}^{-1}$ for all the lines under study. The n value slightly varies from 0.74 to 1.15 for the lines with $J = 8 - 43$ with the mean value equal to 0.985. It should be noted that calculations and measurements have been done only for lines with $\Delta K_a = 0$ and $\Delta K_c = 1$. In principle, the exponent may differ from this value for transitions of other types. Qualitatively the temperature dependence coincides with that for water vapor molecule lines in short-wave region²³ but it differs from this for the lines of H_2O absorption bands corresponding to transitions from low states.²⁴

TABLE IV. Coefficients of the O₃ line shifts (mK/atm) caused by N₂ pressure for 2ν₁ band.

J'	K' _a	K' _c	J''	K'' _a	K'' _c	S ₂			S ₁	Shift	
						dq	qq	pol		Calc.	Exper.
25	6	20	26	7	19	0.001	0.078	1.55	-3.92	-2.29	-1.9
28	5	23	29	6	24	0.076	0.033	1.33	-3.86	-2.42	-1.7
14	7	7	15	8	8	-0.010	0.087	1.42	-3.20	-1.70	-1.8
28	4	24	29	5	25	-0.129	-0.005	0.85	-3.66	-2.95	-1.5
24	4	20	25	5	21	0.004	-0.014	1.06	-3.64	-2.59	-1.7
29	3	27	30	4	26	0.268	0.175	1.80	-3.35	-1.11	-1.2
13	3	11	14	4	10	0.063	-0.047	1.02	-3.11	-2.07	-2.8
43	1	43	44	0	44	0.001	-0.013	0.18	-2.69	-2.51	-2.5
42	0	42	43	1	43	0.001	0	0.21	-2.69	-2.48	-3.4
18	2	16	19	3	17	-0.043	-0.013	0.39	-2.93	-2.60	-2.4
32	0	32	33	1	33	0.006	0.006	0.35	-2.70	-2.34	-2.2
37	4	34	38	3	35	0.211	0.007	2.20	-3.29	-0.87	-1.7
25	1	25	26	0	26	-0.003	-0.008	0.38	-2.70	-2.33	-1.2
25	2	24	26	1	25	-0.025	-0.046	1.55	-2.80	-1.31	-2.7
17	1	17	18	0	18	-0.014	-0.030	0.84	-2.62	-1.82	-2.1
12	0	12	13	1	13	0.041	0.081	-0.19	-2.47	-2.54	-1.7
15	2	14	16	1	15	-0.044	-0.082	2.81	-2.66	0.03	-2.3

TABLE V. Coefficients of the O₃ line shifts (mK/atm) caused by N₂ pressure for 2ν₃ band.

J'	K' _a	K' _c	J''	K'' _a	K'' _c	S ₂			S ₁	Shift	
						dq	qq	pol		Calc.	Exper.
8	8	0	9	9	1	-0.027	-0.264	1.84	-5.46	-3.91	-4.8
21	8	14	21	9	13	-0.029	-0.113	0.12	-6.33	-6.35	-7.0
26	6	20	26	7	19	-0.015	-0.087	0.56	-6.66	-6.20	-6.2
18	6	12	18	7	11	-0.001	-0.088	0.28	-6.06	-5.87	-5.2

DISCUSSION

The above calculations and comparison with the experiment show that, on the whole, the simple ATC method is quite acceptable, at least for estimating the shifts of vibrational-rotational absorption lines of ozone. It was shown that short-range acting polarization potentials contribute to the formation of line shifts more strongly compared to the potential of dipole-quadrupole interaction which can be neglected. At the same time as our calculations and data available from the literature show the contributions of electrostatic interactions into the broadening coefficients are significant. It is known that vibrational effects only weakly contribute to broadening of the ozone spectral lines caused by the oxygen and nitrogen pressure.²⁵ The measured line shifts for three bands presented in the tables demonstrate strong vibrational dependence of the shift coefficients. In order to reach coincidence of calculational and measurement data on shift coefficients it appeared necessary to take into account the vibrational dependence of some components of the polarizability tensor of ozone and to use a fitting procedure to determine the polarizability of a molecule in the excited vibrational states. It is also worth noting that fitting of the parameters of intermolecular potential (of its short-range acting part, i.e., atom-atom interaction potential) happened to be necessary for calculating coefficients of line broadening caused by nitrogen and oxygen pressure, since the parameters of short-range acting potential are unknown.²⁵

Thus one can easily arrive at a conclusion that there exists a certain difference in mechanisms responsible for formation of shifts and widths of the ozone absorption

lines what necessarily should be taken into account when compiling a database of line shifts or making comparison between measured and calculated data.

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