

Calculation of broadening coefficients for H₂O absorption lines in the range from 13550 and 13950 cm⁻¹

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Received March 2, 2005

The pressure broadening coefficients for 164 H₂O lines calculated for the cases of air, nitrogen, and oxygen as foreign gases as well as self-broadening coefficients are presented. The Anderson–Tsao–Curnutte (ATC) technique modified to allow for intermolecular interactions and Maxwell distribution of molecules over the relative velocities was used in the calculations. A good agreement with experimental results has been obtained for all H₂O lines considered. Comparison of results obtained by the ATC method and the method based on complex Robert–Bonamy formalism (CRBF) has shown that in the case of strong collisions both of these methods give close results.

Introduction

Parameters of the water vapor spectral line shapes in the visible and near-infrared ranges are of a significant practical interest, because solar radiation absorption in these ranges determines the atmospheric radiation balance. Earlier,^{1,2} the contribution of H₂O weak absorption lines was estimated; and it was shown that the contribution of weak lines due to transitions to high-excited rotation-vibration states can reach several percent and must be taken into account in calculations of atmospheric radiation fluxes.

In sensing vertical profiles of atmospheric gas concentrations, the absorption line half-widths must be known with an accuracy no worse than 5%, because this parameter essentially determines the absorption function within a given spectral range.³ Therefore, to be sufficiently reliable, the initial spectroscopic information used in calculations must take into account the dependence of broadening coefficients on different intramolecular interactions, vibrational and rotational quantum numbers, and temperature.

Presently available spectroscopic databases (for example, HITRAN⁴ and Schwenke linelist⁵) include calculated values for hundreds of thousands of atmospheric gas lines. Mostly, these are the broadening coefficients for lines belonging to low rotation-vibration molecular bands. The need in the broadening coefficients of H₂O lines belonging to high vibration-rotation bands is not yet properly satisfied.

In this paper, calculated coefficients for H₂O absorption lines belonging to 3ν₁ + ν₃, 2ν₁ + 2ν₂ + ν₃ bands broadened by nitrogen, oxygen, air, and H₂O pressure are presented. In our calculations we used one of the variants of semi-classical collisional broadening theory, the Anderson–Tsao–Curnutte method⁶ modified to allow for distribution over molecular velocities and the dependences of intramolecular characteristics and intermolecular parameters of the absorbing molecule on the vibrational quantum numbers.⁷

1. Theoretical analysis

In terms of the semi-classical collisional broadening theory (the ATC method⁶), the half-width of an absorption line is written as follows

$$\gamma(i, f) = \frac{n}{c} \sum_j \rho(j) \int_0^\infty F(v) v dv \left[\frac{b_c^2}{2} + \int_{b_c}^\infty S_2(i, f, b, v) b db \right]. \quad (1)$$

where i and f make up the set of vibrational and rotational quantum numbers of the initial and final states of the transition; n is the concentration of disturbing particles; c is the speed of light; $\rho(j)$ is the population of the j th energy level of the disturbing molecule; $F(v)$ is the Maxwell distribution of molecules over the relative velocities of colliding particles; b_c is the interruption parameter; $S_2(i, f, b, v)$ is the Anderson interruption function for collision with the impact parameter b and relative velocity v . The interruption function $S_2(i, f, b, v)$ is determined by the electrostatic part of the intermolecular potential and contains information on the energy spectrum, multipole moments, and other characteristics of the colliding molecules

$$S_2(i, f, b, v) = \frac{4}{45} \frac{1}{(hvb^3)^2} \times \sum_j D(jj'|2) \left\{ \sum_{i'} D(ii'|1) \varphi(k_{ii'jj'}) + \sum_{f'} D(ff'|1) \varphi(k_{ff'jj'}) \right\}. \quad (2)$$

In Eq. (2), the dipole-quadrupole interaction (collision between H₂O and non-polar molecule) is taken into account and the following notations are used: $D(jj'|2)$ are the strength of quadrupole transitions in the disturbing molecule; $D(ii'|1)$, $D(ff'|1)$ are the strengths of dipole transitions in the absorbing molecule. The resonance function $\varphi(k_{ii'jj'})$ depends on the parameter $k_{ii'jj'}$ determined by the

collision parameters b and v and by the difference between the energy levels of virtual transitions in absorbing and disturbing molecules

$$k_{ifj\bar{j}} = \frac{2\pi cb}{v}(E_i - E_{\bar{i}} + E_j - E_{\bar{j}}). \quad (3)$$

Here $E_i - E_{\bar{i}}$, $E_j - E_{\bar{j}}$ are differences between the energy levels of virtual transitions in absorbing and disturbing molecules. The resonance parameter $k_{ifj\bar{j}}$ for the upper state of the transition can be obtained by replacing in Eq. (3) the subscript i for f . Analysis of the formulas shows that the difference ($E_{\bar{i}} - E_{\bar{j}}$) in Eq. (3), affecting the line half-width, depends on the rotational and centrifugal constants.

It was shown in Ref. 7 that variation of H₂O rotational and centrifugal constants in highly-excited bending states can reach tens times (Δk -effect, centrifugal effect). The error in the computation conducted for line half-widths of the $4\nu_2$ band in approximation that the energy levels of the upper vibrational state are taken the same as in the ground state reaches 17%. The strengths of the dipole transition $D(f\bar{f}|1)$ [Eq. (2)], determined mainly by the H₂O dipole moment mean value, significantly affect the line half-width. The error in the computation conducted for line half-widths of the $4\nu_2$ band in approximation that the line strengths of the upper vibrational state are taken as for the ground state reaches 80%. On the whole, the ATC computations show that effects of intermolecular dynamics result in a significant (up to 39%) narrowing of some H₂O absorption lines of the $5\nu_2$ band and must be taken into account in calculations of line half-widths formed by transitions to highly excited vibrational states.

The H₂O–N₂ line half-widths calculated by the quantum Fourier theory (QFT) method are presented in Ref. 8; in Ref. 9, calculations by the ATC method for the case of self-broadening are reported. In both of these cases the calculations were made in the approximation of energies of the ground vibrational state. Ignoring the Δk -effect, centrifugal effect in calculations^{8,9} resulted in a 20% deviation from the experimental data, which exceeds the accuracy (5%) required in half-width calculations.³

2. Results and discussion

The air-broadened H₂O half-widths were calculated by the formula

$$\gamma_{\text{air}} = 0.79\gamma_{\text{N}_2} + 0.21\gamma_{\text{O}_2}. \quad (4)$$

The spectroscopic constants for H₂O molecule were obtained from solution of the inverse problem for diagonalization of the effective rotational Watson Hamiltonian with the use of measured¹⁰ energy levels. The account of random resonances was conducted with the use of mixing coefficients for the H₂O wave functions¹¹ in calculating the matrix elements of the effective dipole moment operator.¹²

The mean dipole moment of the H₂O molecule for vibrational states (301) and (221) was calculated using the dipole moment derivatives from Ref. 13.

The calculated results are presented in Fig. 1 and compared with the data from Ref. 14.

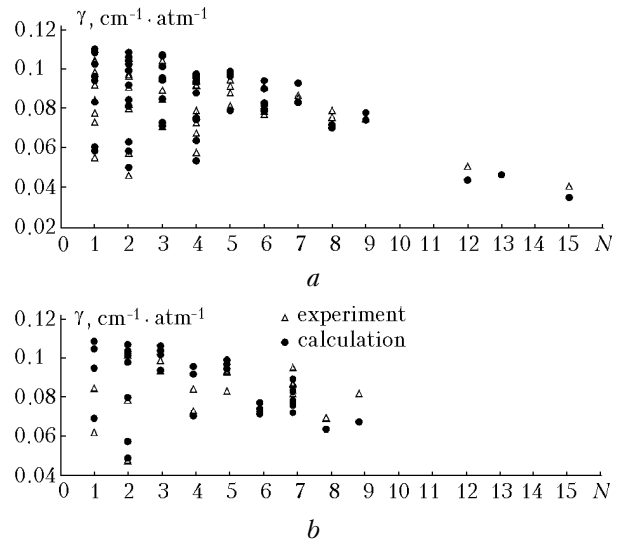


Fig. 1. Broadening coefficients for H₂O lines of $3\nu_1 + \nu_3$ (a) and $2\nu_1 + 2\nu_2 + \nu_3$ (b) bands at air-broadening depending on quantum number $N = J + K_a - K_c + 1$.

The measurements have been carried out with a spectrometer with a dye laser; the measurement error was equal to $0.003 \text{ cm}^{-1} \cdot \text{atm}^{-1}$. Comparison of the calculated and experimental data shows the standard deviation in 65% of measurements to be not higher than 15%. The agreement between experimental and calculated data worsens as the quantum number $N = J + K_a - K_c + 1$ of the low transition state increases, i.e., for lines with high values of rotational quantum numbers J and K_a . A significant narrowing of lines with large N values is seen in Fig. 1.

The calculated coefficients for self-broadened H₂O lines are presented in Fig. 2 together with measured values.¹⁵

The measurement error is $0.006 \text{ cm}^{-1} \cdot \text{atm}^{-1}$, a standard deviation of calculated values from the measured does not exceed 15% in 50% of measurements. The agreement between calculated and measured data worsens as the quantum number $N = J + K_a - K_c + 1$ increases, i.e., for lines with high values of rotational quantum numbers J and K_a . A half-width decrease at increasing N is well seen.

A comparison of mean values of line half-widths for γ values measured in Refs. 14 and 15, γ_{ATC} values calculated by us, and γ_{CRBF} values calculated in Ref. 16 is presented in Table 1. As is seen, the measured and calculated values are rather close; in the cases of broadening by nitrogen and oxygen they coincide within the measurement error. In the case of self-broadening, the agreement between calculated and measured mean values is not good, possibly, because of the large measurement error.

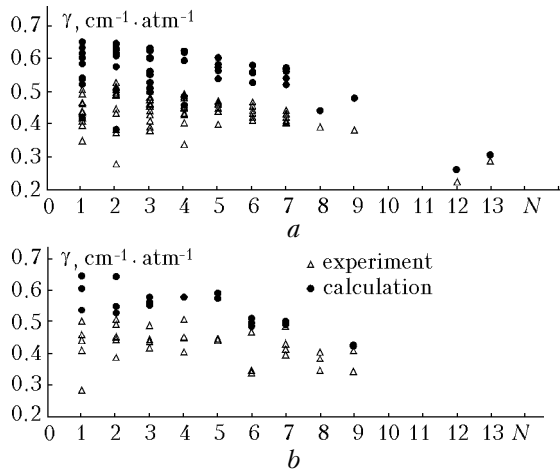


Fig. 2. Broadening coefficients for H₂O lines of 3v₁ + v₃ (a) and 2v₁ + 2v₂ + v₃ (b) bands at self-broadening depending on quantum number N = J + K_a - K_c + 1.

Table 1. Comparison of mean values of broadening coefficients for H₂O lines broadened by pressure of air, nitrogen, oxygen, and H₂O in 3v₁ + v₃ and 2v₁ + 2v₂ + v₃ bands

$\gamma_{\text{mean}}, \text{cm}^{-1} \cdot \text{atm}^{-1}$	Air	N ₂	O ₂	H ₂ O
$\gamma(301)$	0.0859	0.0952	0.0583	0.434
$\gamma_{\text{ATC}}(301)$	0.0856	0.0942	0.0544	0.5538
$\gamma_{\text{CRBF}}(301)$		0.0976	0.0579	
$\gamma(221)$	0.0838	0.0903	0.0567	0.423
$\gamma_{\text{ATC}}(221)$	0.0857	0.0943	0.0529	0.5401
$\gamma_{\text{CRBF}}(221)$		0.0934	0.0569	

The calculations of the broadening coefficients for H₂O lines belonging to 3v₁ + v₃ and 2v₁ + 2v₂ + v₃ bands by use of the complex Robert–Bonamy formalism have been discussed in Ref. 16. In terms of this method, the half-width is determined by the expression¹⁷

$$\gamma = \frac{n\bar{v}}{2\pi c} \sum_j \rho(j) \times \int_0^\infty 2\pi b db \{1 - \exp[-\text{Re} S_2(b)] \cos[S_1(b) + \text{Im} S_2(b)]\}, \quad (5)$$

where v is the mean velocity of thermal motion of the of colliding molecules.

A good agreement with the experiment¹⁴ for H₂O–N₂ and H₂O–O₂ line half-widths was obtained in Ref. 16. A comparative analysis of peculiarities of CRBF and ATC models and our calculated broadening coefficients with those from Ref. 16 has shown the following.

First, in the framework of the CRBF method, the contribution of the isotropic part of intermolecular interactions $S_1(b)$ into line half-width is taken into account explicitly, Eq. (5). Note that in terms of the ATC method, the contributions to the half-width from $S_1(b)$ and $\text{Im} S_2(b)$ are accounted for as well, but not explicitly, i.e., in finding the interruption parameter $b_c < b$ in solving the Anderson interruption equation

$$\text{Re} S_2(b) + |\text{Im} S_2(b) + S_1(b)| = 1. \quad (6)$$

Second, in the framework of CRBF method, $\text{Re} S_2(b)$ (5) contains contributions to the half-width from electrostatic interactions and the short-range part of the potential in contrast to the ATC method, in which $S_2(b)$ [Eq. (2)] contains only electrostatic interactions (dipole-quadrupole for the observed case of H₂O–N₂, H₂O–O₂ collisions).

In the ATC method, the interruption procedure (6) and introduction of the interruption parameter b_c eliminate to some extent the problem on the account of the contribution from the short-range part of the potential, because it is assumed that in collisions with the impact parameter $b_c < b$ the absorption process is interrupted and the H₂O molecule passes to another energy state.

The comparative analysis of contributions to the half-widths from electrostatic and short-range forces¹⁸ has shown that in the case of strong collisions (when the colliding molecules with large multipole moments interact at long distances) the contribution of short-range part of the potential is negligibly small, therefore, the results calculated by the ATC and CRBF methods must be rather close.

The results of comparison for H₂O–N₂ line broadening coefficients calculated by ATC and CRBF methods¹⁶ are given in Table 2, where γ_1 are ATC-calculated half-width values and γ_2 are CRBF-calculated ones with

$$\Delta = \left| \frac{\gamma_1 - \gamma_2}{\gamma_1} \right| \times 100\%$$

as a standard deviation.

Table 2. Comparison of broadening coefficients for H₂O–N₂ lines of 3v₁+v₃ and 2v₁+2v₂+v₃ bands calculated by ATC (γ_1) and CRBF (γ_2) methods

$JK_a K_c - J' K'_a K'_c$	$\gamma_1, \text{cm}^{-1} \cdot \text{atm}^{-1}$	$\gamma_2, \text{cm}^{-1} \cdot \text{atm}^{-1}$	$\Delta, \%$
3v ₁ + v ₃			
6 ₁₅ –5 ₁₄	0.1049	0.102	2.4
6 ₂₅ –5 ₂₄	0.0925	0.091	1.6
5 ₃₂ –4 ₃₁	0.0971	0.098	0.9
7 ₁₆ –7 ₁₇	0.0796	0.081	0.6
5 ₂₃ –4 ₂₂	0.1080	0.106	1.9
5 ₁₄ –4 ₁₃	0.1100	0.107	2.7
4 ₂₂ –3 ₂₁	0.1078	0.107	0.7
4 ₁₃ –3 ₁₂	0.1118	0.109	0.8
5 ₂₄ –5 ₀₅	0.0966	0.099	2.4
4 ₂₃ –4 ₀₄	0.1052	0.107	1.7
3 ₂₁ –2 ₂₀	0.1070	0.108	0.9
2v ₁ + 2v ₂ + v ₃			
1 ₀₁ –2 ₀₂	0.1183	0.118	0.5
2 ₁₂ –3 ₁₃	0.1103	0.110	0.3
3 ₁₃ –4 ₁₄	0.1068	0.106	0.7
7 ₁₇ –8 ₁₈	0.0622	0.062	0.3
4 ₀₄ –5 ₀₅	0.1029	0.101	1.8
2 ₂₁ –3 ₂₂	0.0999	0.104	0.5
3 ₃₁ –3 ₃₀	0.0779	0.085	0.7
5 ₁₄ –6 ₁₅	0.1027	0.100	2.7

The analysis shows that the differences for individual lines from 3v₁ + v₃ and 2v₁ + 2v₂ + v₃ bands can reach 2.4–2.7%; for 80% of lines they do not exceed 1%.

Third, the CRBF calculations in Ref. 16 were performed in approximation of the mean thermal velocity (5). In this paper the ATC method was used with account for the Maxwell distribution over relative velocities of the colliding molecules [Eq. (1)]. It is well known¹⁹ that the mean thermal velocity approximation introduces a 1 to 5% error in calculating H₂O–N₂ line half-widths (v_2) by this method.

On the whole, the comparison of the broadening coefficients for H₂O–N₂ lines ($3v_1 + v_3$ and $2v_1 + 2v_2 + v_3$ bands) (see Table 2) calculated by different methods shows that these give close results in the case of strong collisions. The comparison between the half-width mean values for H₂O–N₂ and H₂O–O₂ lines, calculated by the ATC and CRBF methods, and the experimental ones (see Table 1) demonstrates a good agreement.

Conclusion

In this paper, broadening coefficients for 164 H₂O lines belonging to $3v_1 + v_3$ and $2v_1 + 2v_2 + v_3$ bands and broadened by nitrogen, oxygen, and H₂O have been calculated. The coefficients for air-broadening were found by formula (4). In calculations, the ATC method modified to allow for the intramolecular interactions (Δk -effect, centrifugal effect, vibration dependence of the dipole moment mean values, random resonances) and Maxwell distribution over relative velocities of colliding molecules were used.

Statistical analysis and comparison with the experimental data^{14,15} show that the account of all effects of intermolecular dynamics and distribution of molecules over the motion velocities, in the framework of the ATC method, allows reconstructing of broadening coefficients for H₂O lines from high vibrational bands to be made accurate to the experimental errors. The half-width values obtained can be used in calculations of the atmospheric transmission.

Acknowledgments

The author thanks Dr. A.D. Bykov for fruitful discussion and criticism.

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