

Shift of H₂O absorption lines in the range from 13550 to 13950 cm⁻¹

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Received July 28, 2005

We present data on calculated shift coefficients for 186 H₂O lines shifted by the pressure of air, nitrogen, oxygen, and water vapor. The calculations have been performed using Anderson–Tsao–Curnutte (ATC) technique taking into account the intramolecular interactions, the polarization part of intermolecular potential, and the Maxwell distribution of molecules over relative velocity. Statistical analysis of the results calculated demonstrates a good agreement with the experimental data. The equations derived allow one to estimate the line shifts using calculated line half-widths. The comparative analysis of data obtained using the ATC and complex Robert–Bonamy formalism (CRBF) methods shows that the difference between the calculated results does not exceed 10%. The inverse problem on reconstructing the vibrationally dependent parameters of the isotropic part of polarization interactions from measured line shifts has been formulated for the first time.

Introduction

Measurements and calculations of the shift coefficients for water vapor spectral lines in the near-IR and visible regions are very important for the atmospheric spectroscopy. The neglect of line shifts may lead to significant errors in calculating the atmospheric transmission of narrowband laser radiation.¹ In Ref. 2 it was also shown that the neglect of line shifts might lead to an error of 30% at a height of 20 km in the case of sensing water vapor using DIAL method.

The absorption of solar radiation by water vapor in the near-IR region is known to affect the radiation budget of the atmosphere. In Refs. 3 and 4, the contribution of weak H₂O absorption lines was estimated and it was shown that the contribution of weak lines caused by transitions to states with high values of the rotational quantum number J and “hot” transitions to high-excited vibrational states can reach several percent and should be taken into account in calculating radiative fluxes in the atmosphere. That is why the detailed study of shift coefficients is also of interest. The calculation of shift coefficients and comparing those with the experimental values allow us to refine the intermolecular potential and to improve the calculation technique and approximations used to calculate line half-widths and their temperature dependence.

In Ref. 5 it was shown that, in calculating the shift coefficients for H₂O lines, it is necessary to consider intramolecular interactions, because these significantly influence the calculated results. In Ref. 6, the temperature dependence of the shift coefficients was calculated for the line peaking at 14397 cm⁻¹ and it was shown that the neglect of this dependence may lead to an error higher than 22% at

a height of 10 km in calculating the atmospheric absorption function.

New spectroscopic data banks compiled by now (Partridge and Schwenke, Ref. 7, 0–25000 cm⁻¹, $J \leq 50$) include calculated positions and intensities of more than 300 000 000 lines. Obviously, such a set of data enables one to perform detailed analysis of H₂O spectra in almost any spectral region, being of interest for atmospheric optics. To extend the field of application, these data banks should be complemented with reliable data on line broadening and shift coefficients.

In this paper we present analysis of the shift coefficients for absorption lines of the H₂O bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ in the cases of self-pressure-induced shift and shift induced by pressure of nitrogen, oxygen, and air. The calculations have been performed using a modified Anderson–Tsao–Curnutte (ATC) technique, which is complemented, unlike the traditional one,⁸ with the consideration of effects of intramolecular dynamics, the polarization part of the intermolecular potential, and the Maxwell distribution of molecules over relative velocity of the colliding molecules. In addition, the comparative analyses of data obtained using the ATC and CRBF techniques and of the model used for determination of the H₂O molecule polarizability have been performed.

1. Theoretical analysis

To calculate the line shift coefficients, we have made use of one of the versions of the semiclassical theory of the collision broadening, namely, the ATC technique, which uses the approximation of classical straight-line trajectories. In Refs. 9 to 12, the ATC technique was complemented with the consideration of the polarization part of the intermolecular

potential, the effects of intramolecular dynamics upon the vibrational excitation of the absorbing molecule, and the distribution of molecules over velocity. References 9 to 12 present the calculation technique, the calculated shift coefficients for the H₂O absorption lines shifted by pressure of O₂, N₂, CO₂, H₂, SO₂, air, noble gases, and water vapor, as well as the comparison with the available experimental data. Within the modified ATC technique, the line shift is described by the equation

$$\delta_{if} = \frac{n}{c} \sum_j \rho(j) \int_0^\infty F(v) v dv \int_{b_c}^\infty \{\text{Im} S_2(b, v) + S_1(b, v)\} b db. \quad (1)$$

Here i and f make up the set of vibrational and rotational quantum numbers of the initial and final states of a transition; n is the concentration of buffer particles; c is the speed of light; $\rho(j)$ is the population of the j th energy level of a buffer molecule; $F(v)$ is the Maxwell distribution of colliding particles over relative velocity; b_c is the cut-off parameter; $\{\text{Im} S_2(b, v) + S_1(b, v)\}$ is the imaginary part of the effectiveness function for collision with the impact parameter b and the relative velocity v . The second-order efficiency function $\text{Im} S_2(b, v)$ is determined by the anisotropic part of the intermolecular potential and includes the frequencies and probabilities of the rotational transitions, associated with the dipole and quadrupole selection rules. For the considered case of the dipole-quadrupole interaction between an H₂O molecule and molecules of N₂ and O₂ we have

$$\begin{aligned} \text{Im} S_2(b, v) = & \\ = \frac{4}{45} \frac{1}{(hvb^3)^2} \sum_j D(jj'|2) & \left\{ \sum_i D(ii'|1) \text{Im} f_{12}(k_{iijj'}) - \right. \\ & \left. - \sum_j D(ff'|1) \text{Im} f_{12}^*(k_{ff'jj'}) \right\}, \quad (2) \end{aligned}$$

where $D(ii'|1)$, $D(ff'|1)$ and $D(jj'|2)$ are the strengths of dipole and quadrupole transitions in the absorbing and buffer-gas molecules;

$$D(ii'|1) = \langle v_i | \mu | v_i \rangle L^{vi}(ii') F^{vi}(ii'); \quad (3)$$

$\langle v_i | \mu | v_i \rangle$ are the matrix elements of the H₂O dipole moment; $L^{vi}(ii')$ are the line strengths of the rotational transitions; $F^{vi}(ii')$ are the so-called F -factors, accounting for the vibrational-rotational interaction. The complex resonance function of the dipole-quadrupole interaction, $f_{12}(k_{iijj'}) = \text{Re} f_{12}(k_{iijj'}) + i \text{Im} f_{12}(k_{iijj'})$, depends on the resonance parameter $k_{iijj'}$, determined by the impact parameters b , v , and by the frequencies of virtual transitions:

$$k_{iijj'} = \frac{2\pi cb}{v} (\omega_{i\bar{i}} + \omega_{jj'}) = \frac{2\pi cb}{v} (E_i - E_{\bar{i}} + E_j - E_{j'}). \quad (4)$$

The resonance parameters $k_{ff'jj'}$ can be found by substituting subscripts f for i in Eq. (4).

In Ref. 13 it is shown that the rotational and centrifugal distortion constants of a molecule in high-excited bending vibrational states may vary by several tens and hundreds times as compared to the ground vibrational state. For example, the rotational constant A increases 1.5 times in the state (020) and 3 times in the state (050) as compared to its value in the state (000). The centrifugal distortion constant Δ_k increases 3.5 times in the state (020) and 180 times in the state (050). The vibrational excitation and the change of the rotational and centrifugal distortion constants lead to a significant rearrangement of the rotational energy spectrum and to the change of wave functions of the absorbing molecule. Consequently, the line shifts may vary significantly and even alternate the sign. The calculations accounting for the Δk -effect and the centrifugal distortion have shown that the shift of H₂O lines changes by tens percent for the lines of the bands nv_2 ($n = 1, \dots, 5$); for some lines, it may alternate the sign. Figure 1 shows the H₂O–N₂ shift coefficients for three lines as functions of the vibrational quantum number v_2 . One can see that the vibrational excitation can change both the value and the sign of the shift coefficients, which is explained by the competition among contributions coming from rotational transitions with different frequencies (4) to the line shift.

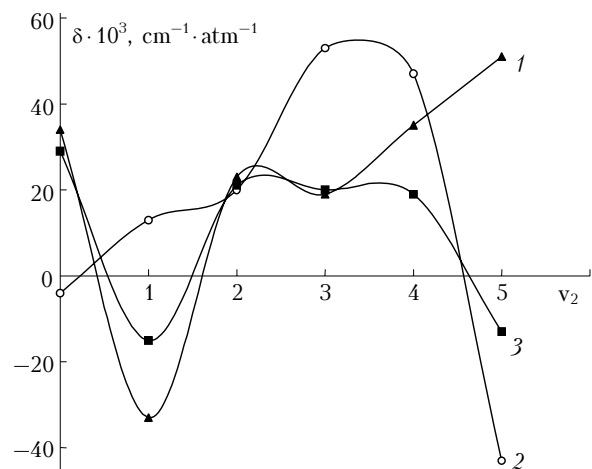


Fig. 1. Effect of intramolecular interactions on the shifts of H₂O–N₂ lines of the bands nv_2 ($n = 0, 1, \dots, 5$): $1_{11}-2_{02}$ (1), $5_{51}-6_{42}$ (2), $8_{36}-9_{09}$ (3).

The first-order efficiency function $S_1(b, v)$ is determined by the isotropic part of the intermolecular potential; in the simplest approximation, it includes the contributions of the polarization (inductive and dispersion) interactions:

$$\begin{aligned} S_1(b, v) = \frac{3\pi}{8hvb^5} \times \\ \times \left\{ \alpha_2 \{ \mu_i^2 - \mu_f^2 \} + [\mu_2^2 + \frac{3}{2} \frac{\epsilon_1 \epsilon_2}{(\epsilon_1 + \epsilon_2)} \alpha_2] \{ \alpha_i - \alpha_f \} \right\}. \quad (5) \end{aligned}$$

Here μ_i , μ_f are the mean dipole moments of the absorbing molecule in the initial and final vibrational states of a transition; α_i , α_f are the mean polarizabilities of the absorbing molecule; μ_2 , α_2 are the mean dipole moment and the mean polarizability of the buffer molecule; ε_1 , ε_2 are the ionization potentials of the absorbing and the buffer molecules. The analysis of Eq. (5) shows that the change of the dipole moment and polarizability in the upper state due to vibrational excitation may significantly affect the value and the sign of the line shift. In Refs. 9 and 12, it was found that a 10% increase of the polarizability of the H₂O molecule in the high-excited states (301) and (221) leads to a increase of $S_1(b, \nu)$ by 10 to 15 times and the contribution of this term to the H₂O–N₂ line shift may exceed 75% for the lines of the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$. The sign of the shift by pressure of nonpolar molecules becomes negative in this case.

It should be noted that the neglect of the effects of vibrational excitation (neglect of the growing contribution from $S_1(b, \nu)$ [Eq. (5)] at the increasing polarizability of H₂O in high vibrational states) may lead to a significant error in the value and the sign of the shift. In Ref. 14, the shifts of some lines of the $3\nu_1 + \nu_3$ band due to H₂O–N₂ collisions were calculated by the Quantum Fourier Transform (QFT) and ATC techniques. However, it should be noted that none of the calculation techniques gives correct results, if the contribution from the isotropic part of the polarization interactions (5) to the shift is neglected.

2. Results and discussion

We present shift coefficients calculated of for 186 H₂O absorption lines of the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ in the cases of shifting by pressure of

nitrogen, oxygen, and water vapor. The calculations have been performed with the use of a modified ATC technique Eqs. (1)–(5). The shift of H₂O lines by pressure of the air δ_{air} is determined as

$$\delta_{\text{air}} = 0.79\delta_{\text{N}_2} + 0.21\delta_{\text{O}_2}. \quad (6)$$

The spectroscopic constants of the H₂O molecule were obtained in Ref. 15 by solving the inverse problem through the diagonalization of the effective rotational Watson Hamiltonian with the use of the energy levels measured in Ref. 16. Diagonal matrix elements of the dipole moment operator were calculated taking into account Fermi and Darling–Dennison accidental resonances with the use of the mixing coefficients of vibrational wave functions of the H₂O molecule.¹⁵ The mean dipole moment of the H₂O molecule in the vibrational states (301) and (221) was calculated with the use of the dipole moment derivatives from Ref. 17. The mean polarizability of H₂O molecule in the vibrational states (301) and (221) was determined from the least-squares fitting of the calculated line shifts due to H₂O–air collisions to the measured ones.⁹ The fitting was performed for three lines of this band; the shifts of other lines of this band, and the shifts induced by the pressure of other buffer gases (N₂, O₂, and self-induced shift) were calculated using the obtained value of the polarizability. The mean polarizability of the H₂O molecule is equal to 15.90 in the vibrational state (301) and 15.94 (in units of 10^{–25} cm³) in the state (221).

The calculated H₂O–air shift coefficients for lines of the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ are shown in Figs. 2 and 3 along with the experimental data.¹⁸ The mean uncertainty of the measurements is 0.003 cm^{–1}·atm^{–1}. The rms deviation of the calculated values from the measured ones is 1.5·10^{–3} cm^{–1}·atm^{–1}, and the standard deviation does not exceed 15% for 65% of the measured values.

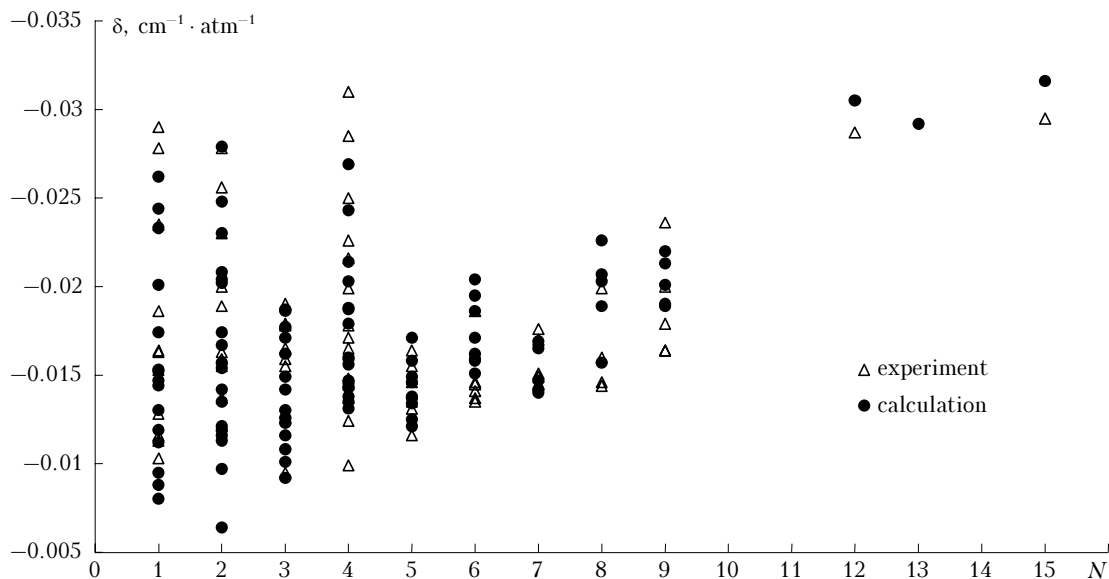


Fig. 2. Shift coefficients for lines of the H₂O band $3\nu_1 + \nu_3$ in the case of air-pressure-induced shift as functions of the quantum number $N = J + K_a - K_c + 1$.

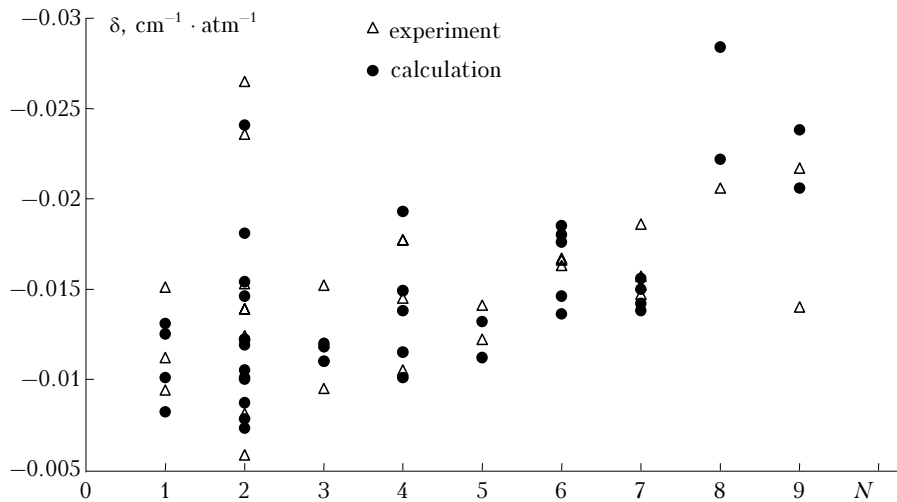


Fig. 3. Shift coefficients for lines of the H₂O band $2\nu_1 + 2\nu_2 + \nu_3$ in the case of air-pressure-induced shift as functions of the quantum number $N = J + K_a - K_c + 1$.

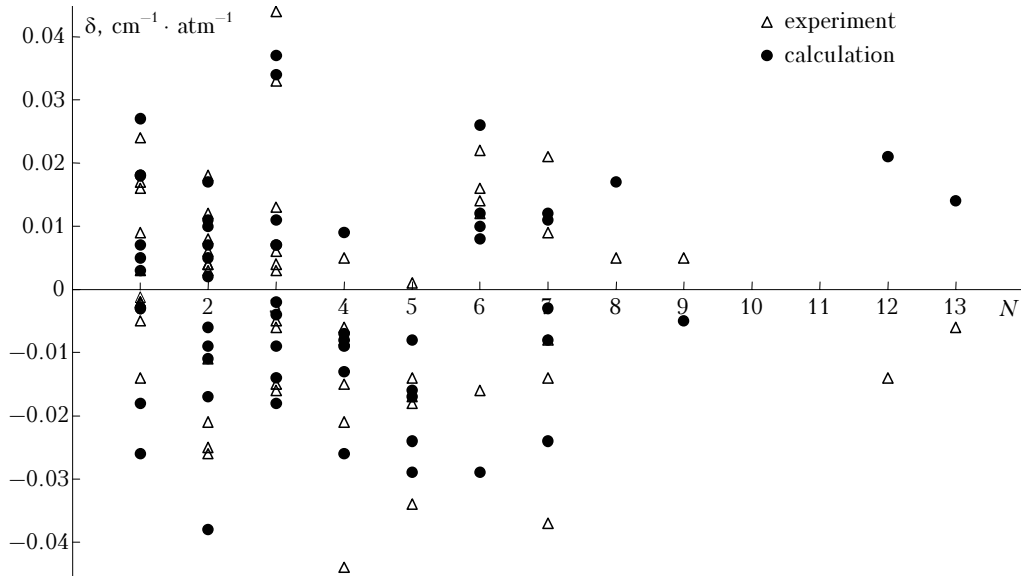


Fig. 4. Shift coefficients for lines of the H₂O band $3\nu_1 + \nu_3$ in the case of self-induced shift as functions of the quantum number $N = J + K_a - K_c + 1$.

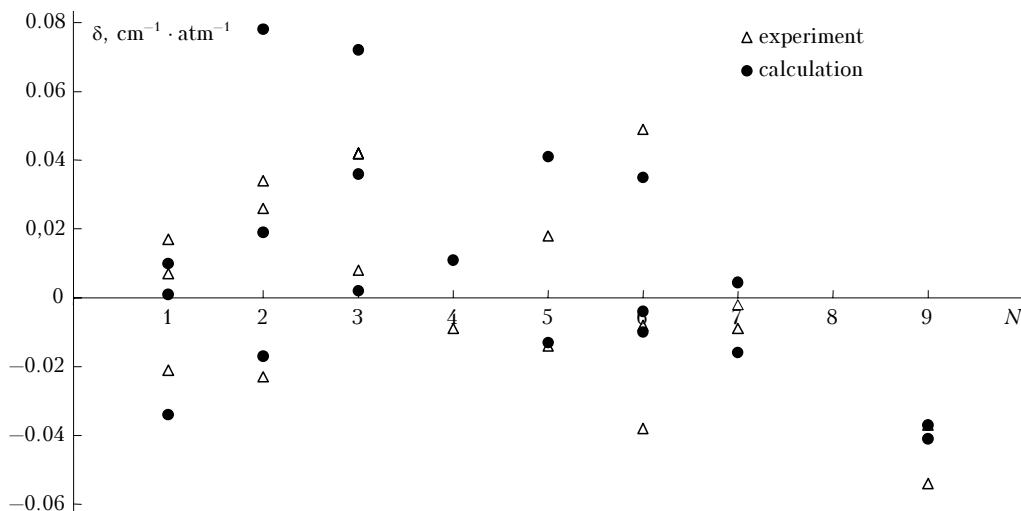


Fig. 5. Shift coefficients for lines of the H₂O band $2\nu_1 + 2\nu_2 + \nu_3$ in the case of self-induced shift as functions of the quantum number $N = J + K_a - K_c + 1$.

The calculated H₂O–H₂O shift coefficients for lines of the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ are shown in Figs. 4 and 5 compared with the experimental values from Ref. 19. The experimental uncertainty is $0.005 \text{ cm}^{-1} \cdot \text{atm}^{-1}$. The rms deviation of the calculated values from the measured ones is $1.26 \cdot 10^{-2} \text{ cm}^{-1} \cdot \text{atm}^{-1}$; the standard deviation does not exceed 15% for 50% of the measured values.

It can be seen from Figs. 2 and 3 that the H₂O line shift coefficients in the case of air-pressure-induced shift have minus sign and their absolute value increases monotonically with the increase of the quantum number $N = J + K_a - K_c + 1$ of the lower state of a transition. In Figs. 4 and 5, we can notice that the shift alternates the sign as a function of the quantum number $N = J + K_a - K_c + 1$ of the lower state of a transition.

2.1. Comparison of ATC and CRBF techniques

It was shown in Ref. 12 that minus sign of the H₂O shift coefficients in the case of shifting by pressure of nitrogen, oxygen, and air is caused by the dominant contribution of the adiabatic shift of levels. The analysis carried out in Ref. 12 shows that more than 75% of the H₂O shift coefficient value in the case of shifting by pressure of nonpolar molecules is determined by the contribution coming from $S_1(b)$ [Eq. (5)]: the larger the difference between the polarizability of the H₂O molecule in the lower and upper vibrational states, the larger the contribution from this term to the line shift. Table 1 compares the mean values of shift coefficients for the cases of the H₂O–N₂, H₂O–O₂, and H₂O–air mixtures. The first row presents the mean values of the experimental¹⁸ shift coefficients δ_{exp} for lines of the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$; the second and third rows present the mean values δ_{ATC} calculated in this work by the ATC technique; the fourth and fifth rows present the mean values δ_{CRBF} calculated by the CRBF technique.²⁰

Table 1. Comparison of the mean values of the H₂O shift coefficients in the case of shifting induced by pressure of nitrogen, oxygen, and air in the bands $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$

$\delta_m, \text{ cm}^{-1} \cdot \text{atm}^{-1}$	N ₂	O ₂	Air
δ_{exp}	–0.0133	–0.0261	–0.0166
$\delta_{\text{ATC}}(301)$	–0.01262	–0.03192	–0.01668
$\delta_{\text{ATC}}(221)$	–0.01041	–0.02848	–0.01421
$\delta_{\text{CRBF}}(301)$	–0.01465	–0.02519	–
$\delta_{\text{CRBF}}(221)$	–0.01136	–0.01707	–

It can be seen from Table 1 that both of the calculation techniques provide for a good agreement with the experimental values in the case of the H₂O–N₂ shift. In the case of oxygen-induced shift, δ_{CRBF} agrees with δ_{exp} poorer than δ_{ATC} . It should be noted that in Ref. 20 no fitting parameters were used, while in this paper the fitting parameter is the polarizability of the H₂O molecule in the upper vibrational state.

The calculations have shown that the self-induced pressure shift coefficients of H₂O lines oscillate, that is, the sign of the shift may be different for lines with different rotational quantum numbers (Figs. 4 and 5). This is explained by the fact that the H₂O molecule has large dipole moment (1.87 D in the ground vibrational state); therefore, the dipole-dipole interaction dominates, and the second-order term $\text{Im}S_2(b)$ [Eq. (2)] is the major contributor to the line shift. Thus, in the case of self-broadening the shift is determined by the nonadiabatic mixing of states and by the balance of energies of rotational transitions (4) in the initial and final vibrational states. As a consequence, the sign of the shift coefficient can be both plus and minus, because it is determined by the sign of the resonance parameter k [Eq. (4)] of the transition, responsible for the largest contribution.

In the CRBF technique, the line shift coefficient is determined by the following equation:

$$\delta = \frac{n\bar{v}}{2\pi c} \sum_j \rho(j) \times \int_0^{\infty} 2\pi b db \{ \exp[-\text{Re}S_2(b)] \sin[S_1(b) + \text{Im}S_2(b)] \}. \quad (7)$$

Here \bar{v} is the mean thermal velocity of colliding molecules. CRBF is a cut-off-free technique, taking into account the contributions to the line shift from both the imaginary and real parts of the efficiency function $S_2(b)$. It should be noted, that in the ATC technique the contributions to the broadening and shift from both parts of $S_2(b)$ are also taken into consideration through the solution of the modified cut-off equation:

$$\text{Re}S_2(b) + |\text{Im}S_2(b) + S_1(b)| = 1. \quad (8)$$

In the CRBF technique, $S_2(b)$ [Eq. (7)] accounts for the contributions from electrostatic interactions and the short-range part of the potential, as well as for bending of the trajectory upon the collision. At the same time, in the ATC technique, $S_2(b, v)$ [Eq. (2)] includes only electrostatic interactions (dipole-quadrupole interaction for the considered case of collisions of H₂O molecules with N₂ and O₂) and the approximation of straight-line trajectories is used in it. However, in the ATC technique, the cut-off procedure (8) and the use of a fitting parameter removes, to a great extent, the problem of accounting for the contribution from the short-range part of the potential.

The calculations performed in Refs. 9 to 12 have shown that the contribution to the shift of lines of the $\nu_1 + 3\nu_3$ band from $S_1(b, v)$ [Eq. (5)] exceeds that from $\text{Im}S_2(b, v)$ [Eq. (2)] by the order of magnitude. The consideration of the short-range repulsion forces is likely needed in the calculations of half-widths and shifts of lines with the high value of the rotational quantum number J , belonging to the low vibrational states. In Ref. 21 it was shown that

for the case of the so-called “strong” collisions (when the colliding molecules have high multipole moments and interact at long distances) the contribution of the short-range part of the potential is small. In this case, the results given by the ATC and CRBF techniques are close.

The results of our comparison of the H₂O–N₂ line shifts calculated by the ATC and CRBF²⁰ techniques are summarized in Table 2, where δ_1 is the shift calculated by the ATC technique, δ_2 is the shift calculated by the CRBF technique, and Δ is the standard deviation of one calculation from another:

$$\Delta = \left| \frac{\delta_1 - \delta_2}{\delta_1} \right| \cdot 100\%.$$

The analysis shows that for 80% of lines the differences between the calculations do not exceed 10%.

Table 2. H₂O–N₂ shift coefficients for lines of the $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ bands calculated by the ATC (δ_2) and CRBF (δ_1) [Ref. 22] techniques

$JK_aK_c - J'K'_aK'_c$	$\delta_1, \text{cm}^{-1} \cdot \text{atm}^{-1}$	$\delta_2, \text{cm}^{-1} \cdot \text{atm}^{-1}$	$\Delta, \%$
	$3\nu_1 + \nu_3$		
5 ₁₄ –4 ₁₃	–0.014	–0.0129	7.8
4 ₂₂ –3 ₂₁	–0.010	–0.0091	9
4 ₂₃ –3 ₂₂	–0.012	–0.0110	8.3
4 ₀₄ –3 ₀₃	–0.014	–0.0127	9.3
4 ₁₄ –3 ₁₃	–0.013	–0.0127	2.3
5 ₃₂ –5 ₃₃	–0.014	–0.0128	8.5
1 ₁₁ –2 ₁₂	–0.009	–0.0083	7.7
2 ₁₂ –3 ₁₃	–0.009	–0.0082	8.8
2 ₂₀ –3 ₂₁	–0.009	–0.0099	8.8
3 ₂₂ –4 ₂₃	–0.013	–0.0122	6.1
4 ₂₂ –5 ₂₃	–0.011	–0.0120	9
	$2\nu_1 + 2\nu_2 + \nu_3$		
5 ₃₂ –5 ₃₃	–0.011	–0.0098	10
3 ₃₀ –3 ₃₁	–0.013	–0.0127	2.3
3 ₃₁ –3 ₃₀	–0.012	–0.0124	3
5 ₄₁ –5 ₄₂	–0.018	–0.0186	3.3
5 ₄₂ –5 ₄₁	–0.017	–0.0166	2.3
2 ₁₂ –3 ₁₃	–0.007	0.0069	2.8
4 ₁₄ –5 ₁₅	–0.009	–0.0084	6.6
4 ₀₄ –5 ₀₅	–0.007	–0.0065	7.1
5 ₀₅ –6 ₀₆	–0.010	–0.0090	10
6 ₁₆ –7 ₁₇	–0.015	–0.0136	9.3

It should be noted that in Ref. 20 the shifts of H₂O lines were calculated by the CRBF technique in the approximation of the average relative velocity. In Ref. 12, the influence of this approximation on the calculated results on the H₂O–N₂ shift coefficients was analyzed and it was shown that the corresponding error can be as high as 20–25%. To obtain the needed accuracy of calculation, the Maxwell distribution of molecules over relative velocity should be taken into account.

Equation (5) is known to be valid only in the Born–Oppenheimer approximation, when the electron and nuclear motions can be separated approximately. The correction for the deviation from the Born–Oppenheimer approximation is usually small for the low vibrational states, namely, it is on

the order of λ^4 , where $\lambda = \sqrt{B/\omega}$ (for H₂O $\lambda \sim 0.1$). For high-excited vibrational states, the correction is expected to increase.

It should be noted that Eq. (5) is valid only in the London approximation,²² when the expression in braces can be presented as a sum of two terms (inductive C_6^{ind} and dispersion C_6^{disp}), and the dispersion part of the potential is approximately expressed through the polarizability of the H₂O molecule in an excited vibrational state:

$$C_6^{\text{disp}} = \frac{3}{2} \frac{\varepsilon_i \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \alpha_2 (\alpha_i - \alpha_f). \quad (9)$$

The accuracy of this approximation is likely low; as was mentioned in Ref. 23, the error reaches 10% for the case of the atomic interaction. In the calculations of Ref. 20, the same approximation (5) for the isotropic part of the polarization potential is used as in the calculations by the ATC technique in Ref. 9 and in this paper. However, in our calculations, the differences ($\alpha_i - \alpha_f$) are fitted to the experimentally measured line shifts, while in Ref. 20 the value of ($\alpha_i - \alpha_f$), obtained in the *ab initio* calculations, is used.

It should also be emphasized that the approximation (5) ignores the contribution from the isotropic part of the atom-atom potential. Indeed, the main part of the atom-atom correction to the interaction potential depends on the intermolecular separation as R^{-6} ; the dependence of its isotropic part is obviously the same. Thus, the contribution from the atom-atom potential to the line shift must be the same as that from the polarization potential. It seems that the use of fitting parameters in the CRBF technique should refine the calculated line shift coefficients.

A very important result of the calculations performed in this paper and in Refs. 5, 9, and 10 is the determination of the “transferability” property of the fitting parameter ($\alpha_i - \alpha_f$). As follows from the calculated results, this parameter, determined from the experimental data for one pair of molecules, for example H₂O–N₂, can be then used for calculating the coefficients of pressure-induced shifts in the case of other buffer gases, in particular, noble gases,⁵ CO₂, H₂O, and H₂ [Ref. 10].

2.2. Correlation between coefficients of line broadening and shift

Since the pressure-induced line shifts for H₂O molecules in high-excited vibrational states is determined, in the case of nonpolar buffer molecules, by the adiabatic effect, leading to the monotonic dependence on quantum numbers, a correlation is observed between the line half-width and shift values. This correlation can be expressed as a linear regression $\delta = a\gamma + b$, where the coefficients a and b were determined from the least squares fit to the

calculated values. For the $3\nu_1 + \nu_3$ band the correlation is expressed by the following equations:

$$\begin{aligned}\delta_{N_2} &= 0.152\gamma_{N_2} - 0.0265, \\ \delta_{O_2} &= 0.633\gamma_{O_2} - 0.0658.\end{aligned}\quad (10)$$

For the $2\nu_1 + 2\nu_2 + \nu_3$ band, the dependence has the form

$$\begin{aligned}\delta_{N_2} &= 0.262\gamma_{N_2} - 0.0436, \\ \delta_{O_2} &= 0.831\gamma_{O_2} - 0.0764.\end{aligned}\quad (11)$$

Equations (10) and (11) allow one to estimate the line shift coefficient, if the line half-width is known, and this may appear to be useful in some cases. In Ref. 18, a correlation was found between the measured shift and half-width values:

$$\begin{aligned}\delta_{N_2} &= 0.336\gamma_{N_2} - 0.0448, \\ \delta_{O_2} &= 0.631\gamma_{O_2} - 0.0640.\end{aligned}\quad (12)$$

The linear regression coefficients in Eq. (12) are determined from the fitting of all the measured line half-widths and shifts in the range from 13550 to 13950 cm^{-1} . Since this range includes lines of three bands: $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$, and $2\nu_1 + 2\nu_3$, Eq. (12) from Ref. 18 is less accurate than Eqs. (10) and (11).

2.3. Determination of the vibrational dependence of the isotropic part of the potential

As was mentioned above, the polarizability of the H_2O molecule in the excited vibrational state α_f was determined by fitting the calculated shift coefficients to the measured ones for three lines of each vibrational band. The value of the polarizability determined in this way was used to calculate the shifts for other lines and the shifts induced by pressure of other buffer gases. This method of determination of the polarizability was proposed for the first time in Ref. 9. Then it was used by other authors, in particular, to calculate half-widths by the CRBF technique.²⁰

Since this technique, being based on a certain approximation, gives quite satisfactory results it seems useful to analyze it and determine the possibility of its further improvement, allowing one to find the parameters, determining the vibrational dependence of the isotropic part of the polarization interactions, from the measured shift coefficients.

The isotropic part of the intermolecular potential can be presented as a series

$$V^{\text{iso}}(R, q) = \frac{C_6(q)}{R^6} + \frac{C_7(q)}{R^7} + \frac{C_8(q)}{R^8} + \dots, \quad (13)$$

where the coefficients are functions of normal vibrational coordinates q . In the approximation of small vibrations, these coefficients can also be represented as a series:

$$C_n(q) = C_n^{(0)} + \sum_a C_n^{(a)} q_a + \sum_{a \leq b} C_n^{(ab)} q_a q_b + \dots \quad (14)$$

To take into account the intramolecular interactions yielding anharmonicity of vibrations and accidental resonances, it is necessary to use the equations of the method of contact transformations and to obtain the "effective" parameters $\tilde{C}_n(q)$. Then, using standard methods and calculating the difference between the mean values (14), we can obtain the following equation for the first-order cut-off function:

$$S_1(b, v) = S_{1,ip}(b, v) - S_{1,fp}(b, v) = \sum_n \left[\langle v_i | C_n(q) | v_i \rangle - \langle v_f | C_n(q) | v_f \rangle \right] \frac{1}{\hbar} \int_{-\infty}^{\infty} dt R^{-n}; \quad (15)$$

$$\begin{aligned}\langle v | C_n(q) | v \rangle &= C_n^{(0)} + \sum_{b=1}^3 C_n^{(aa)} - \\ &- \sum_b \frac{C_n^{(a)} k_{abb}}{\omega_b} - (1 - \delta_{b3}) \frac{3C_n^{(a)} k_{aaa}}{\omega_a} (v^a + 1/2).\end{aligned}\quad (16)$$

Here k_{abc} are anharmonicity constants.

According to the above equations and the analysis, the most shift coefficients of the water vapor absorption lines from the bands in the near-IR and visible regions are determined by the first and second derivatives of the isotropic part of the potential with respect to the normal coordinates and linearly depend on the vibrational quantum numbers. On the one hand, this obviously allows the calculation of the isotropic part of the potential to be made, if the coefficients of the series (14) are known.

On the other hand, according to Eqs. (15) and (16) the parameters $C_n^{(0)}$, $C_n^{(a)}$, $C_n^{(ab)}$ can be determined from the measured shifts of lines of several vibrational bands. In this case, the term $S_2(b, v)$, determined by the anisotropic part of the intermolecular potential (dipole-quadrupole interaction in our case), should be calculated by the known dependence of the mean dipole moment on vibrational quantum numbers.

Conclusions

This paper presents calculated results on the line shift of 186 H_2O absorption lines of the $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ bands in the case of shift induced by pressure of nitrogen, oxygen, and water vapor. The calculations were performed with the use of a modified ATC technique, accounting for the effects of intramolecular dynamics, the contribution from the isotropic part of polarization interactions, and the Maxwell distribution of molecules over relative velocity. A good agreement between calculated and the experimental values of the shift coefficients^{18,19} has been demonstrated. A comparative analysis of the ATC and CRBF techniques has been performed. It

has been shown that for the case of strong collisions the results calculated by different techniques differ by no more than 10%. The linear regression equations (10) and (11), obtained in this work, allow the estimation of the line shifts for the $3\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ bands to be done for the $\text{H}_2\text{O}-\text{N}_2$ and $\text{H}_2\text{O}-\text{O}_2$ mixtures. The inverse problem on the determination of the vibrationally dependent parameters of the isotropic part of the intermolecular potential from the measured H_2O line shifts has been formulated for the first time.

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