

Broadening and shift coefficients of H₂O line centers under strong vibrational excitation

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The influence of intramolecular effects (the anomalous centrifugal effect, variations of mean dipole moment, and the polarizability) on relaxation parameters of H₂O lines broadened by N₂ pressure at strong vibrational excitation of the molecule has been investigated. Calculations were performed within the framework of spectral lines impact theory, when both real and imaginary parts of the interruption function were taken into account. To improve the convergence of the perturbation theory series for matrix elements of the effective rotational Watson Hamiltonian, the Pade–Borel method of divergent series summation was used. The calculated half-widths and shifts of H₂O line centers were compared with the experimental ones for 3ν₁ + ν₃ band.

Calculations and measurements of broadening and shift coefficients of water vapor spectral lines in the near IR and the Visible are of particular interest for atmospheric optics, because the absorption of solar radiation in this range determines the radiation balance of the atmosphere.¹ Numerous experimental and theoretical investigations of H₂O line broadening have already been conducted to the present time.² The calculated and measured data were included into well-known databases HITRAN and GEISA.^{3,4}

The available estimates^{5,6} indicate that contribution of weak H₂O absorption lines, which were not included into the databases, can reach several percents. These extremely weak lines with an intensity less than 10⁻²⁸ cm/mol are connected with transitions either to the states with high rotational quantum number ($J > 20$ for the ground and the first excited vibrational states) or to highly-excited vibrational states. Due to a large number of such transitions, their total contribution is of significance for visible and near UV ranges and should be taken into account in calculations of radiation flows in the atmosphere. Thus, it is necessary to determine half-widths and shifts of water vapor weak absorption lines connected with the transitions between highly excited vibrational-rotational (VR) states.^{7,8}

The transitions to high rotational and vibrational states in H₂O molecule are connected with strong intramolecular interactions. In the method of effective Hamiltonians strong intramolecular interactions cause numerous vibrational and vibrational-rotational (VR) resonances, and anomalously large centrifugal corrections. It is important that in practice calculations lead to divergence of the series, representing matrix elements of the effective Hamiltonian. In this case, calculated energy levels and wave functions, used for calculation of line strengths and transition frequencies in semiclassical line broadening impact theory can be significantly distorted.^{9,10} As a consequence, half-

widths and shifts of line centers also can be distorted and differ significantly from the experimental values.

An alternative calculation method, taking into account all intramolecular effects, is the variation one.¹¹ The calculation results for H₂O broadening and shift coefficients, presented in Ref. 12, used matrix elements of the dipole moment, determined with variational wave functions. It was also shown that anharmonicity of vibrations and centrifugal distortion can significantly change the half-widths and shifts of individual lines.^{13–16}

In the method of effective Hamiltonians, which is much simpler (in calculation sense) than the variational one, an alternative way of calculation is the use of the summation method of the divergent series (in particular, the method of Pade–Borel). It was earlier successfully applied in calculations of H₂O energy levels.^{9,10}

In this work we consider the influence of strong centrifugal effect on relaxation parameters of H₂O spectral lines of high VR-bands. Unlike earlier calculations of energy levels and wave functions^{13–16} we took into account the calculation divergence for highly excited states in the method of effective Hamiltonians. The Pade–Borel method is used for the elimination of the divergence.¹⁰ In addition, the anomalous centrifugal effect, the change of mean dipole moment, and H₂O polarizability in high VR states, as well as real and imaginary parts of interruption function are taken into consideration. We also compare calculated and experimental values of broadening and shift coefficients of the lines.¹⁷ Calculated and measured values of relaxation parameters were compared for lines of 3ν₁ + ν₃ band, corresponding to strong collisions, for which the influence of trajectory distortion and the contribution of short-range components of intermolecular potential are small.¹⁸ The influence of strong centrifugal effect is studied using bands of $n\nu_2$ type as an example at excitation from 1 to 12 quanta of the bending vibration.

Calculation results allow a conclusion that anomalously strong centrifugal effect in H₂O molecule (connected with the bending vibration of large amplitude) leads to non-monotonic dependence of line half-widths on the vibrational quantum numbers. At excitation of 1–7 quanta of ν_2 vibrational mode, line narrowing is observed; for higher overtones broadening coefficients increase.

1. Theoretical analysis

In the framework of broadening theory, the line center half-width and shift, corresponding to $i \rightarrow f$ transition, in the impact approximation,^{19,20} are determined by real and imaginary parts of the efficiency function $U(i, f, p, b)$:

$$\gamma_{if} = \frac{m\nu}{c} \sum_p \rho(p) \int_0^\infty \text{Re}U(i, f, p, b) b db; \quad (1)$$

$$\delta_{if} = \frac{m\nu}{c} \sum_p \rho(p) \int_0^\infty \text{Im}U(i, f, p, b) b db. \quad (2)$$

Here

$$\begin{aligned} \text{Re}U(i, f, p, b) &= 1 - \exp\{-\text{Re}S_2^{\text{outer}}(b) - S_2^{\text{middle}}(b)\} \times \\ &\quad \times \cos\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\}; \\ \text{Im}U(i, f, p, b) &= \exp\{-\text{Re}S_2^{\text{outer}}(b) - S_2^{\text{middle}}(b)\} \times \\ &\quad \times \sin\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\} \end{aligned} \quad (3)$$

and approximations of linear trajectories and average speed of collisions are used. In Eqs. (1)–(3) i, f are quantum numbers of initial and final states of transitions; p is the quantum number of a buffer particle; b is the target distance; ν is the average relative speed of colliding particles; $\rho(p)$ is the population of the p level of the broadening molecule.

Further, we take into account the contribution of electrostatic (second order of perturbation theory, $S_2(b) = \text{Re}S_2^{\text{outer}}(b) + i\text{Im}S_2^{\text{outer}}(b) + S_2^{\text{middle}}(b)$) and polarization parts (first order of perturbation theory, $S_1(b)$) of the intermolecular potential. The short-range part of intermolecular interaction is not taken into consideration. As is well known, the calculations conducted in the framework of this approximation give quite satisfactory results for strong collisions,¹⁸ when the minimal distance between approaching molecules is less than interruption parameter b_0 of the Anderson theory.

In first order of perturbation theory, the contribution to relaxation parameters of water molecule lines is determined by isotropic part of the intermolecular potential (induction and dispersion interactions):

$$\begin{aligned} S_1(b) &= \frac{3\pi}{8\hbar\nu b^5} \left\{ \alpha_2 [\langle V_i | \mu_1^2 | V_i \rangle - \langle V_f | \mu_1^2 | V_f \rangle] + \right. \\ &\quad \left. + \frac{3}{2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \alpha_2 [\langle V_i | \alpha_1 | V_i \rangle - \langle V_f | \alpha_1 | V_f \rangle] \right\}. \end{aligned} \quad (4)$$

Here μ_1, α_1 are the dipole moment and H₂O polarizability; α_2 is the polarizability of N₂ in the ground vibrational state; $\varepsilon_1, \varepsilon_2$ are the ionization potentials of H₂O and N₂; $|V_i\rangle, |V_f\rangle$ are vibrational wave functions of H₂O initial and final states, respectively.

In second order of the perturbation theory the contribution to relaxation parameters of H₂O line at the broadening by nitrogen pressure is determined by the dipole-quadrupole interaction:

$$\begin{aligned} S_2^{\text{outer}}(b) &= \frac{16}{45} \frac{1}{(\hbar\nu b^3)^2} \sum_{p'} D(pp' | 2) \times \\ &\quad \times \left\{ \sum_{i'} D(i'i' | 1) \varphi_{12}(k_{ii'pp'}) + \sum_{f'} D(ff' | 1) \varphi_{12}^*(k_{ff'pp'}) \right\}. \end{aligned} \quad (5)$$

In Eq. (5), $D(i'i' | 1)$ and $D(pp' | 2)$ are dipole and quadrupole forces of lines (reduced matrix elements) of the exciting and absorbing molecules, respectively; $\varphi_{12}(k)$ is the complex resonance function for the dipole-quadrupole interaction, the asterisk denotes complex conjugation. The resonance parameter k in Eq. (5) is determined by the balance of energies of rotational levels in lower or upper vibrational states:

$$\begin{aligned} k_{ii'pp'} &= \frac{2\pi cb}{\nu} (E_i - E_{i'} + E_p - E_{p'}), \\ k_{ff'pp'} &= \frac{2\pi cb}{\nu} (E_f - E_{f'} + E_p - E_{p'}). \end{aligned} \quad (6)$$

It is well-known that H₂O molecule belongs to the class of light nonrigid molecules. This causes a strong dependence of different molecular characteristics and parameters of intermolecular interaction on vibrational quantum numbers.⁹ Reduced matrix elements in Eq. (5) and resonance parameters (6) depend on energy levels and wave functions of initial and final states of the transition under consideration, as well as on energy levels and wave functions of the states involved in summation over i', f', p' . As compared to transitions to low VR-states, these values for upper VR-transitions can change, thus changing the half-width and shifts of line centers of upper H₂O VR-bands. It is important to note that excitation of more than three vibrational quanta in H₂O significantly increases the amplitude of atom vibration, thus significantly changing energy levels, wave functions, dipole moments, and polarizability.

In this paper, the influence of these parameters on broadening and shift coefficients is numerically analyzed.

1.1. Measurement of rotational energy spectrum

At vibrational excitation of H₂O the rotational and centrifugal constants change (Δk -effect and centrifugal distortion). This is followed by a change of the rotational energy spectrum of the excited

vibrational state as compared to ground vibrational state, and to changes in $\omega_{ff'} = E_f - E_{f'}$ frequencies in the second equation (6), as well as by a change of dipole transition probabilities $D(ff'|1)$ in the second summand in braces in Eq. (5).

As an example, rotational A , B , C and centrifugal Δ_k constants for vibrational states at bending vibration excitation are given in Table 1.²¹ It is seen that rotational constant A can be increased by 2.7; 10.5; 30.9; 37.1 orders of magnitude at excitation of 5, 7, 10, or 12 vibrational quanta ν_2 . Centrifugal Δ_k constant can increase constantly by orders of magnitude, i.e., by 76, 1173, 104357, 129071 times at the excitation of 5, 7, 10, or 12 quanta of bending vibration. At the same time, rotational constants B and C change no more than by 10% at excitation of 12 bending vibration quanta.

Table 1. Variability of rotational A , B , C , and centrifugal Δ_k constants at excitation of bending vibration in the H_2O molecule²¹

| ν_2 | E_{ν_2} , cm ⁻¹ | A | B | C | Δ_k |
|---------|--------------------------------|---------|-------|------|------------|
| 0 | 0 | 27.83 | 14.51 | 9.28 | 0.028 |
| 1 | 1594 | 31.13 | 14.66 | 9.14 | 0.048 |
| 2 | 3151 | 35.56 | 14.81 | 9.00 | 0.098 |
| 3 | 4666 | 42.04 | 14.92 | 8.86 | 0.142 |
| 4 | 6134 | 52.63 | 15.01 | 8.74 | 0.924 |
| 5 | 7542 | 73.87 | 15.05 | 8.63 | 2.13 |
| 6 | 8870 | 130.71 | 15.06 | 8.52 | 6.34 |
| 7 | 10087 | 293.04 | 15.10 | 8.40 | 32.84 |
| 8 | 11254 | 532.08 | 15.50 | 8.23 | 161.5 |
| 9 | 12533 | 674.42 | 16.07 | 8.04 | 211.5 |
| 10 | 13857 | 859.71 | 16.73 | 7.81 | 292.2 |
| 11 | 15295 | 960.913 | 16.19 | 7.94 | 328.4 |
| 12 | 16824 | 1031.23 | 17.56 | 7.71 | 361.4 |

Apparently, strong Δk -effect and anomalous centrifugal effect in upper vibrational states of H_2O molecule must contribute to energy levels of upper vibrational state of transition (6) and lead to changes in half-widths and shifts of line center of VR-bands as compared to the rotational spectrum.

Note that strong centrifugal effect in H_2O causes a poor convergence or even divergence of the series of effective rotational Hamiltonian, which describes the structure of rotational energy spectrum. In this work, to calculate energy levels in (6) and wave functions, the Pade–Borel method of summation of the series of the effective rotational Watson Hamiltonian was used:

$$H = H^{\text{diag}} + \{H^{\text{nondiag}}, J_{xy}^2\}. \quad (7)$$

Here H^{diag} and H^{nondiag} are presented as the series over degrees of operators of the angular moments J^2 and J_z^2 . Summation of H^{diag} series by Pade–Borel method gives¹⁰:

$$H^{\text{diag}} = \int_0^\infty \exp(-z) \frac{U_0 U_1 + (U_1^2 - U_0 U_2)z}{U_1 - U_2 z} dz. \quad (8)$$

Coefficients U_n in Eq. (8) can be found through rotational and centrifugal constants of effective rotational Hamiltonian (7):

$$U_0 = \left(A - \frac{B+C}{2}\right)J_z^2 + \frac{B+C}{2}J^2, \quad (9)$$

$$U_1 = -\Delta_j J^4 - \Delta_{jk} J^2 J_z^2 - \Delta_k J_z^4,$$

$$2U_2 = H_k J_z^6 + H_{kj} J^2 J_z^4 + H_{jk} J^4 J_z^2 + H_j J^6.$$

Transformation of non-diagonal part of Hamiltonian (7) is made in the same way:

$$H^{\text{nondiag}} = \int_0^\infty \exp(-z) \frac{T_0 T_1 + (T_1^2 - T_0 T_2)z}{T_1 - T_2 z} dz. \quad (10)$$

Expansion coefficients (10) are defined in the following way:

$$T_0 = \frac{B-C}{4}, \quad (11)$$

$$T_1 = -\delta_j J^2 - \delta_k J_z^2,$$

$$T_2 = h_k J_z^4 + h_{jk} J^2 J_z^2 + h_j J^4.$$

The use of Eqs. (8)–(11) eliminates the errors caused by the divergence of the effective rotational Hamiltonian series.

1.2. Change of H_2O mean dipole moment and polarizability

The excitation of bending vibration in H_2O molecule causes an increase of the mean value of the angle between OH bonds. Mean value of the dipole moment significantly increases as the molecule configuration approaches to the linear one. In particular, mean dipole moment decreases for (010), (020), ..., (070) states, however, it increases again during further excitation. Thus, the mean dipole moment in the states, corresponding to bending vibration excitation, behaves non-monotonically, acquiring the lowest value close to the barrier to linearity ($\nu_2 = 7$). This is proved by calculations of matrix elements of the H_2O dipole moment with variational wave functions²² (Fig. 1). At the same time, a slight increase of mean dipole moment is observed when exciting valence vibrations (quantum numbers ν_1 and ν_3).²²

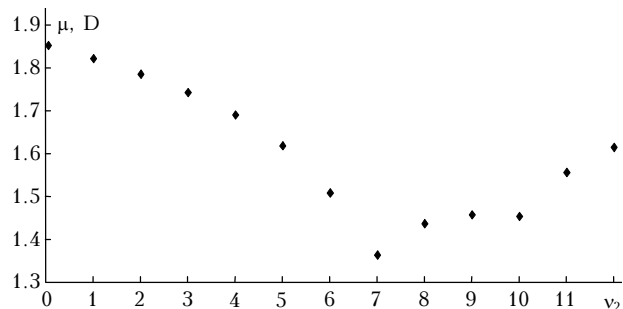


Fig. 1. The dependence of H_2O mean dipole moment on the number of quanta of the bending vibration.²²

Calculations of line half-widths of H₂O–N₂ bending bands $n\nu_2$ ($n = 0, 1, \dots, 5$) in the framework of Anderson theory with effective rotational Watson Hamiltonians¹³ demonstrate the line narrowing during the increase of the number of quanta of the bending vibration. It was found that half-width decrease can reach 39% in the $5\nu_2$ band as compared to the rotational band.

Mean values of the molecule polarizability, determining the contribution of adiabatic level shift (4) in the line center half-width and shift, also change during vibrational excitation. In this paper we use the estimates of H₂O average polarizability by the formula¹⁵:

$$\alpha(\nu_1\nu_2\nu_3) = \alpha_e + \alpha_1\nu_1 + \alpha_2\nu_2 + \alpha_3\nu_3. \quad (12)$$

Here α_e is the H₂O polarizability in the ground state. Expansion coefficients (12) are determined in Ref. 15 from solving the inverse problem: $\alpha_1 = 0.270 \pm 0.024$, $\alpha_2 = 0.178 \pm 0.036$, $\alpha_3 = 0.390 \pm 0.025$.

As it was shown in Ref. 23, at excitation of ν_1 , ν_3 vibrations, an increase in line half-widths (approximately by 12% in the $6\nu_1$ band as compared to the rotational band) is observed due to the increase of polarizability in excited states. Thus, adiabatic shift of levels at collisions, determined by the difference of mean polarizabilities in Eq. (4), leads to an increase in broadening coefficient of lines and a significant change in shift coefficients.

A variant of Robert–Bonamy theory of impact broadening with rotational Watson Hamiltonian was used in Ref. 23. Earlier, broadening and shift coefficients for the H₂O line centers were calculated^{13–16} with the use of Anderson theory and effective rotational Watson Hamiltonian. However, joint influence of all factors of H₂O vibrational excitation (retuning of the rotational spectrum, non-monotonous behavior of the mean dipole moment, and the increase of polarizability) on line center half-width and shift was not studied.

Thus, preliminary analysis has shown that the main factors of H₂O intramolecular dynamics, influencing the half-width, are the change in rotational energy spectrum, caused by the Δk -effect and centrifugal distortion, as well as the change in molecular characteristics, i.e., mean dipole moment and polarizability at a strong vibrational excitation. The change in the mean polarizability has the strongest effect. As a consequence, half-width and shift of the same H₂O lines induced by N₂ pressure in $n\nu_2$ and ν_1 , $3\nu_1 + \nu_3$ bands may differ in magnitude by tens of percents and even in sign in case of line center shifts. The significant dependence of H₂O shift coefficients on vibrational quantum numbers was shown earlier in calculations^{13–16,23} and proved experimentally.^{15,17}

2. Results and discussion

The preliminary analysis shows that different factors of intramolecular interactions differently affect

half-width and shift of water vapor lines, either increasing or decreasing them. To draw more accurate conclusions, the influence of H₂O vibrational excitation on the broadening and shift coefficients of $3\nu_1 + \nu_3$ (bending vibration is not excited) and $n\nu_2$ bands (only bending vibration is excited) was numerically analyzed. During this process, all main factors were taken into account, i.e., centrifugal effect, change in dipole moment, and mean polarizability. We also considered the case of the broadening induced by nitrogen pressure and made a comparison with experimental data.¹⁷

2.1. Calculations of half-widths and shifts of H₂O line centers in $3\nu_1 + \nu_3$ band

Calculations of half-widths and shifts of H₂O line centers of $3\nu_1 + \nu_3$ band, induced by the nitrogen pressure, were conducted by Eqs. (1)–(6). Energy levels and wave functions were calculated with effective rotational Hamiltonian (7)–(11). Spectroscopic constants of (301) H₂O state, used in this work, were obtained by O.V. Naumenko. Mean values of H₂O dipole moment, calculated with high-accurate variational wave functions, were also used in calculations.²² The polarizability of (301) H₂O state was determined earlier.¹⁵ Results are presented in Tables 2 and 3.

Table 2. Comparison of calculated and measured half-widths of H₂O–N₂ lines in $3\nu_1 + \nu_3$ band

| $JK_aK_c - J'K'_aK'_c$ | Calculation 1 | Calculation 2 | Experiment |
|------------------------|---------------|---------------|------------|
| 615–514 | 0.1049 | 0.1002 | 0.0965 |
| 532–431 | 0.0971 | 0.1011 | 0.0991 |
| 716–707 | 0.0796 | 0.0823 | 0.0817 |
| 523–422 | 0.108 | 0.1073 | 0.1063 |
| 514–413 | 0.110 | 0.1082 | 0.105 |
| 422–321 | 0.1078 | 0.1066 | 0.1063 |
| 413–312 | 0.1118 | 0.1076 | 0.0965 |
| 524–505 | 0.0966 | 0.1023 | 0.1034 |
| 423–404 | 0.1052 | 0.1034 | 0.0978 |
| 321–220 | 0.107 | 0.1062 | 0.1053 |
| 101–202 | 0.1183 | 0.1177 | 0.115 |
| 212–313 | 0.1163 | 0.1182 | 0.1193 |
| 313–414 | 0.1068 | 0.1038 | 0.0989 |
| 717–818 | 0.0622 | 0.0805 | 0.0562 |
| 404–505 | 0.1029 | 0.1012 | 0.0944 |
| 221–322 | 0.0999 | 0.0948 | 0.0935 |
| 331–330 | 0.0779 | 0.0834 | 0.0823 |
| 514–615 | 0.1026 | 0.0988 | 0.0942 |

The comparison of calculation results obtained by the Watson (calculation 1) and Pade–Borel (calculation 2) models is of particular interest.

Note that different methods in calculations of frequency of the rotational transitions in Eq. (5) can differ from 5 to 40 cm^{–1}. For example, for transitions from the levels with $J = 3, 4$ this difference does not exceed 5 cm^{–1}, but it reaches 30–40 cm^{–1} for $J = 7$, $K_a = J$. Therefore, calculated broadening coefficients differ approximately by 15%.

Table 3. Comparison of calculated and measured shifts of H₂O–N₂ lines in 3ν₁ + ν₃ band

| $J K_a K_c - J' K'_a K'_c$ | Calculation 1 | Calculation 2 | Experiment |
|----------------------------|---------------|---------------|------------|
| 414–413 | –0.0129 | –0.0141 | –0.0155 |
| 422–321 | –0.0091 | –0.0098 | –0.0106 |
| 423–322 | –0.0110 | –0.0108 | –0.0105 |
| 404–303 | –0.0127 | –0.0128 | –0.0132 |
| 414–313 | –0.0127 | –0.0131 | –0.0133 |
| 532–533 | –0.0128 | –0.0133 | –0.0142 |
| 111–212 | –0.0083 | –0.0097 | –0.0101 |
| 212–313 | –0.0082 | –0.0088 | –0.0096 |
| 220–321 | –0.0099 | –0.0089 | –0.0085 |
| 322–423 | –0.0122 | –0.0125 | –0.0128 |
| 422–523 | –0.0120 | –0.0128 | –0.0135 |
| 330–331 | –0.0117 | –0.0097 | –0.008 |
| 541–542 | –0.0186 | –0.0196 | –0.0191 |
| 542–541 | –0.0166 | –0.0191 | –0.0176 |
| 414–515 | –0.0084 | –0.0089 | –0.0101 |
| 404–505 | –0.0065 | –0.0069 | –0.0074 |
| 505–606 | –0.0090 | –0.0096 | –0.0116 |
| 616–717 | –0.0136 | –0.0142 | –0.0172 |

The second column of the Table 2 (calculation 1) presents line half-widths calculated with Watson Hamiltonian model, in the third column (calculation 2) are half-widths calculated by the Pade–Borel model, the fourth column presents measured¹⁷ half-widths. Analysis of calculation results has shown that standard deviation from experiment makes up 15% for 65% of lines in calculation 1 and 10% for 90% of lines in calculation 2. Thus, the use of Hamiltonian transformed by the Pade–Borel method (7)–(11) gives more accurate results than the Watson Hamiltonian (7).

The second column in the Table 3 (calculation 1) presents the line half-widths calculated with Watson Hamiltonian, the third column (calculation 2) shows the calculations by the Pade–Borel, the fourth one includes measurements from Ref. 17. Comparison of calculation results with experimental data has shown that standard deviation makes up 15% for 65% of lines in calculation 1 and 10% for 90% of lines in calculation 2. Thus, the use of the Pade–Borel method gives more precise results for H₂O line center half-widths and shifts.

The comparison of Calculation 1, Calculation 2, and the experimental data for half-width of H₂O–N₂ lines in 3ν₁ + ν₃ band is illustrated in Fig. 2.

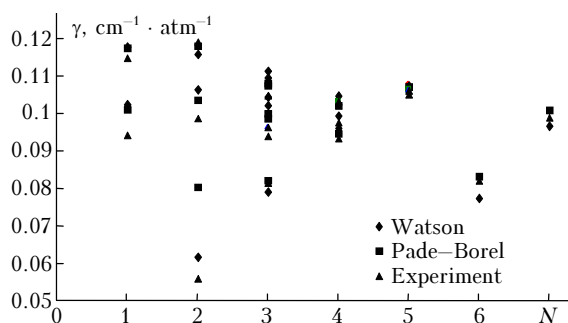
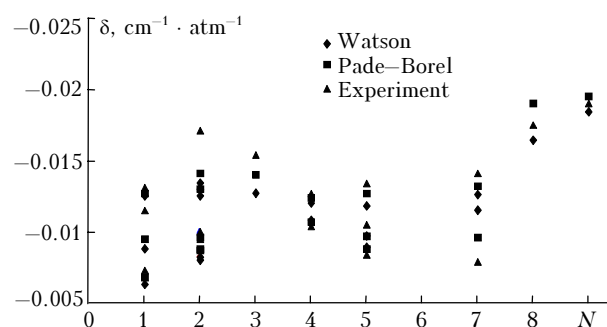
**Fig. 2.** Dependence of H₂O–N₂ line half-width in 3ν₁ + ν₃ band on the quantum number $N = J + K_a - K_c + 1$.

Figure 3 illustrates a comparison of Calculation 1, Calculation 2, and the experimental data for H₂O–N₂ line shifts in 3ν₁ + ν₃ band.

**Fig. 3.** Dependence of H₂O–N₂ line shifts in 3ν₁ + ν₃ band on the quantum number $N = J + K_a - K_c + 1$.

2.2. Vibrational dependence of H₂O line half-widths of nν₂ (n = 0, 1, ..., 12) bending bands

As is well known, an anomalous centrifugal effect is observed in the water molecule, strongly affecting the line position and intensity. Centrifugal distortion changes wave functions and relative position of rotational sublevels, thus changing the frequencies and transition probabilities induced by collisions. In its turn, the change of these parameters can change the coefficients of lines broadening and shift.

Note that a large number of lines in 5ν₂, 6ν₂, and even 10ν₂ bands is observed in water vapor spectrum in near IR and visible regions.²⁴

Earlier,¹³ the centrifugal distortion influence on broadening of band lines of nν₂ (n = 0, 1, ..., 5) type were estimated. It was shown that the distortion can lead to a certain narrowing of spectral lines. However, other effects caused by “soft” bending vibration excitation were not taken into account in Ref. 13. In particular, the change of dipole moment and polarizability in (0n0) states were not taken into consideration. An effective rotational Watson Hamiltonian was used for calculation of energy levels and wave functions. These calculations were conducted by the Anderson–Tsao–Curnutte method.

In this work the calculations are performed by the method described in Refs. 19 and 20, free of interruption approximation. Energy levels and wave functions were determined by Eqs. (8)–(11), where possible calculation divergence, caused by a strong centrifugal effect is taken into account. Mean values of H₂O dipole moment operator, calculated with high-precision wave functions,²² were used. Spectroscopic constants of H₂O bending states were taken from Ref. 21. Mean H₂O polarizability was determined by Eq. (12).

Typical calculation results are illustrated in Fig. 4. They show that the change of line half-widths in bands ν₂, 2ν₂ do not exceed 12–15%, however, for all these lines in 6ν₂, 7ν₂ bands the narrowing can reach 25%. The received calculated values agree well

with the half-width measurements of $3\nu_2$ band² and calculated values for $4\nu_2$, $5\nu_2$ bands.¹³

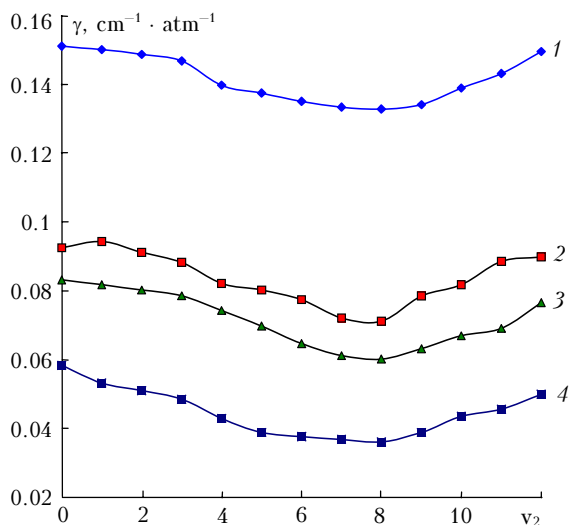


Fig. 4. Dependence of $\text{H}_2\text{O}-\text{N}_2$ line half-widths on ν_2 quantum number of bending vibration: 110–221 (1); 531–660 (2); 713–880 (3); 661–752 (4).

Note that half-widths depend non-monotonically on bending vibration quantum number. An evident correlation between line half-widths and dipole moment mean values in $(0n0)$ states (see Figs. 1 and 4) is observed. For all calculated lines the broadening coefficients are minimal at $n = 7$, the vibrational state (070) turns out to be close in energy to the barrier to linearity of the potential energy function. Mean dipole moment for (070) vibrational state is equal to 1.3 D, which is by 12% less than for the ground vibrational state. Broadening coefficients increase at further excitation of bending vibration for the states higher than the barrier to linearity.

Non-monotonous dependence of broadening coefficients on ν_2 vibrational quantum number can be explained by two main factors. First, the decrease of dipole moment leads to a decrease in the force of dipole-quadrupole interaction and line half-widths. As the molecular polarizability increases negligibly (see Eq. (12)), then the adiabatic part of the half-width also increases insignificantly. Second, a strong change of rotational A and centrifugal Δ_k constants forces the rotational spectrum to look like the spectrum of a flattened symmetric top. In this case only a few rotational transitions can contribute to non-adiabatic part of the half-width. As a consequence, line half-widths decrease at $\nu_2 \leq 7$.

For large values of ν_2 dipole moment increases and so does the polarizability of the molecule. This results in the increase of the broadening coefficients, because the contribution of centrifugal effect for such states does not change any more after reaching its maximum.

Conclusion

In this work, the influence of H_2O intramolecular dynamics and vibrational excitation peculiarities on

broadening and shift coefficients has been considered. Calculation results for the bands of two types were presented: compound bands connected with excitation of valence vibrations $3\nu_1 + \nu_3$ and bending bands $n\nu_2$ ($n = 0, 1, \dots, 12$). The broadening by N_2 is considered, taking into account the main intermolecular interactions and intramolecular factors related to vibrational excitation.

Analysis of calculation results and comparison with the obtained experimental data allow the following conclusions.

Since intramolecular dynamics of highly excited H_2O molecule significantly differs from the dynamics of lower VR-states, a strong dependence of line half-widths on vibrational quantum numbers is observed. The dependence is caused by several factors. For bands related to excitation of valence vibrations only, the main contribution is made by adiabatic effect and the difference in polarizabilities in the excited and ground states.²³ However, for the band lines conditioned by the excitation of bending vibration, centrifugal distortion is of importance. The calculations indicate that centrifugal effect leads to a certain line narrowing.¹³

When calculating half-widths and shifts of H_2O lines of upper VR-bands, one should take into account possible divergence of effective rotational Hamiltonian series. The use of Pade–Borel summation method significantly improves the agreement with experimental values.

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