High-excited rotational states of H_2O. Self-broadening and shifting in the ν_2 band

A.E. Protasevich,[1] S.N. Mikhailenko,[1] and V.I. Starikov[1,2]

[1] *Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk*
[2] *Tomsk State University of Control Systems and Radio Electronics*

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Self-broadening and shift coefficients in the ν_2 band of the H_2O molecule are calculated in two different computational schemes. The calculated values are compared with the experimental ones. It is analyzed how the dependence of the effective dipole moment on the rotational state affects the calculated parameters. The broadening and shift coefficients are calculated using the multi-diagonal form of the molecular Hamiltonian that makes possible obtaining of correct rotation-vibration wave functions for high quantum numbers with allowance for different-type resonance interactions.

Introduction

The water molecule plays the key role in atmospheric absorption of infrared and optical radiation, and knowledge of its spectral characteristics is very important for various applications. Theoretical and experimental methods used in spectroscopy of water vapor were thoroughly considered in Ref. 1.

The theory of broadening and shift of spectral lines is now a well-developed theory with various computational schemes (see, for example, Ref. 2). Nevertheless, it should be emphasized that the progress in experimental and theoretical investigations of broadening and shift coefficients for water vapor spectral lines is not so impressive, as in investigations of line positions and strengths.

The positions of more than 20000 water vapor absorption lines are measured by now in the spectral region from 0 to 25000 cm^{-1}. Lines caused by transitions to highly excited rotational-vibrational states were found in spectra of flame and sunspots; they were assigned, and experimental energy levels with the total quantum number $v_1 + v_2 + v_3 \approx 10$ and the rotational quantum numbers $J \approx 35$, $K_a \approx 32$ were determined.

The situation with self-broadening and shift coefficients for the H_2O molecule is somewhat different. Most publications are connected with the study of these parameters in the region of 1600–2200 cm^{-1} (ν_2 band).

The aim of our investigations is the experimental and theoretical study of self-broadening and shift coefficients for H_2O spectral lines in the region of 2000–6600 cm^{-1}.

In this paper, we describe a method for obtaining correct rotational-vibrational (RV) wave functions of the H_2O molecule, present shift coefficients and line halfwidths in the ν_2 band calculated using two different schemes, and compare these calculations with the available experimental data.

Besides the terms "shift coefficient" and "broadening coefficient," we use the terms "shift parameter," "shift," "broadening parameter," "line halfwidth," and others.

From here on, for brevity, we most often use the terms "shift" and "broadening". It should be kept in mind that in this paper we consider the pressure-induced shift of water vapor absorption lines (shift) and halfwidths of these lines at the pressure of 1 atm (broadening).

Rotational-vibrational molecular Hamiltonian

To calculate line shifts and broadening, we first have to calculate matrix elements of operators of various physical parameters, such as dipole moment of a molecule, polarizability, and so on in the basis of RV wave functions. To obtain the RV wave functions, we use the transformed molecular Hamiltonian $\tilde{H}$ obtained from the initial full molecular RV Hamiltonian by the method of contact transformations. In the general case, the Hamiltonian $\tilde{H}$ can be represented as

$$\tilde{H} = \sum_{V,V'} H_{VV'} |\Psi_V\rangle\langle\Psi_{V'}|, \qquad (1)$$

where $H_{VV'}$ are rotational operators; Ψ_V are vibrational wave functions, and $V \equiv (v_1\ v_2\ v_3)$ is the symbolic notation of a vibrational state.

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The form of Eq. (1) assumes that the vibrational states (V) and (V') are united in a single group (polyad) of interacting states. In the H_2O molecule, two first polyads consist of non-interacting (isolated) vibrational states (000) and (010). They are followed by triads (groups of three vibrational states) {(020), (100), (001)}; {(030), (110), (011)}, etc.[1] Such separation is valid, if we do not consider highly excited rotational energy levels. If these energy levels are included in the consideration, even the ground vibrational state (000) cannot be thought isolated. The most consistent method implies inclusion of all vibrational states needed for analysis of RV transitions in a spectral region under consideration into Eq. (1).

Our immediate task is calculation of the broadening and shift parameters for purely rotational spectral lines and the band ν_2. For this purpose, we united five vibrational states {(000), (010), (020), (100), (001)} into a pentad of interacting states. This allows us to take into account all possible resonance interactions between rotational energy levels of the two lowest vibrational states (000) and (010). Thus, the matrix of the Hamiltonian $\tilde{H}$ in the basis of vibrational wave functions Ψ_V has the form

$$\tilde{H} = \begin{array}{c} \begin{array}{ccccc} (000) & (010) & (020) & (100) & (001) \end{array} \\ \left| \begin{array}{ccccc} H_{11} & H^F_{12} & H^F_{13} & H^F_{14} & H^C_{15} \\ & H_{22} & H^F_{23} & H^F_{24} & H^C_{25} \\ & & H_{33} & H^F_{34} & H^C_{35} \\ & \text{H.c.} & & H_{44} & H^C_{45} \\ & & & & H_{55} \end{array} \right| \end{array}.$$

The designation H.c. stands for the part of the matrix from the Hermitian-conjugate Hamiltonian. The operators $H^F_{VV'}$ describe the interaction between vibrational states of the same symmetry and $H^C_{VV'}$ describe the interaction between vibrational states of different symmetries.

The second peculiarity in the scheme of obtaining molecular wave functions is connected with operator representation $H_{VV} \equiv H^{(V)}$. Usually, $H^{(V)}$ is represented by the reduced form of the rotational Hamiltonian $H^{(V)}_{\text{red}}$ having nonzero matrix elements $< J, K \,|\, H^{(V)}_{\text{red}} \,|\, J, K + \Delta K >$ with $\Delta K = 0, \pm 2$ in the basis of symmetric top rotational wave functions $|\, J, K >$. As was shown in Ref. 3, this form of the Hamiltonian prevents processing of energy levels with high values of rotational quantum numbers. In this paper, we use a multi-diagonal form of $H^{(V)}$ written through the generating functions $F(\mathbf{J}^2, J_z)$ and $\chi_n(\mathbf{J}^2, J_z)$:

$$H^{(V)} = F(\mathbf{J}^2, J_z) + \frac{1}{2}\sum_{n=0}^{4}\{\chi_n(\mathbf{J}^2, J_z), J_+^{2n} + J_-^{2n}\}.$$

The braces denote anticommutator. The functions F and χ_n are taken as series[4] in terms of the elementary generating function G:

$$F(\mathbf{J}^2, J_z) = E_J + \sum_{i,j\neq 0} g_{ij}\mathbf{J}^{2i}G^j(\alpha_0, J_z) \Big/ \left[1 + \sum_{i,j\neq 0} \beta_{ij}\mathbf{J}^{2i}G^j(\alpha_0, J_z)\right];$$

$$\chi_n(\mathbf{J}^2, J_z) = u_0 + \sum_{i,j\neq 0} u_{ij}\mathbf{J}^{2i}G^j(\alpha_n, J_z) \Big/ \left[1 + \sum_{i,j\neq 0} \gamma_{ij}\mathbf{J}^{2i}G^j(\alpha_n, J_z)\right]. \quad (2)$$

The function G has the form[5,6]:

$$G(\alpha_n, J_z) = \frac{2}{\alpha_n}(\sqrt{1 + \alpha_n J_z^2} - 1). \quad (3)$$

In Eqs. (2) and (3), the parameters E_J, u_0, and α_n are the functions of the operator $\mathbf{J}^2$, for example, $E_J = E_0 + u_{10}\mathbf{J}^2 + u_{20}\mathbf{J}^4 + \ldots$. The interaction operators are also used in the non-reduced form, namely,[7,8]

$$H^F_{VV'} = \sum_{lpm} F_{2lm2p}\mathbf{J}^{2l} \times \times [J_+^{2p}(J_z + p)^m + (-1)^m(J_z + p)^m J_-^{2p}]$$

for the Fermi interaction and

$$H^C_{VV'} = \sum_{lpm} C_{2lm2p+1}\mathbf{J}^{2l} \times \times [J_+^{2p+1}(2J_z + 2p + 1)^m + (-1)^{m+1}(2J_z + 2p + 1)^m J_-^{2p+1}]$$

for the Coriolis interaction.

Analysis of the results of processing of all available experimental energy levels ($J \le 35$, $K_a \le 32$) for the pentad under consideration is beyond the scope of this paper. Here, to obtain the wave functions, we used experimental energy levels for J, $K_a \le 25$ for all the five vibrational states.[9–11] A total of $I = 2939$ energy levels were used, for which we obtained the non-weighted rms deviation $\sigma = 0.016$ cm^{-1} and the sum of square deviations for all energy levels $\sum_i^I (E_i^{\text{exp}} - E_i^{\text{cal}})^2 = 0.7$ cm^{-2}. Table 1 presents the mixing coefficients for some rotational energy levels of the vibrational state (010). Starting from $J \approx 19$, the state (010) should be considered together with the neighboring vibrational states. Similarly, starting from $J \approx 21$, the state (000) should also be considered together with the other states (for $J \ge 26$ the mixing coefficients between some rotational energy levels of the states (000) and (010) achieve 50%).

Table 1. Mixing coefficients for some rotational levels of the vibrational state (010)*

J	K_a	K_c	E_{exp} (Ref. 11)	ΔE	%				
					(000)	(010)	(020)	(100)	(001)
19	8	12	7219.889	−9.7	–	70.2	29.4	0.3	0.1
20	14	7	9406.508	−23.2	–	99.2	0.7	0.1	–
20	14	6	9406.474	−19.5	–	99.7	0.3	–	–
21	2	20	6430.686	−30.8	4.1	95.9	–	–	–
21	4	17	7428.758	−48.9	0.4	99.5	0.1	–	–
21	9	13	8418.254	−35.7	–	93.2	6.7	0.1	–
21	14	7	9897.559	−52.2	–	61.2	35.6	3.1	0.1
21	15	7	10218.452	−20.6	–	99.7	0.2	0.1	–
21	15	6	10218.439	−66.2	–	95.1	2.0	2.5	0.4
22	14	8	10407.252	−58.0	–	95.8	3.9	0.3	–
23	10	14	–	–	–	85.5	14.0	0.5	–
23	14	9	–	–	–	61.3	36.2	2.4	0.1
25	0	25	7715.668	−12.0	3.2	96.8	–	–	–
25	1	25	7715.668	−27.7	3.4	96.6	–	–	–

* Energy levels are given in cm^{-1}, $\Delta E = (E_{exp} - E_{cal}) \cdot 10^3$ cm^{-1}, the bar means that assignment of this level is ambiguous.

Calculation of self-broadening and shift of lines in the H_2O ν_2 band

Shifts δ and halfwidths γ of spectral lines were calculated by two methods: the Anderson–Tsao–Curnutte (ATC) method[12] and the Robert–Bonamy (RB) method.[13] In the both computational schemes, the interaction potential included the contributions of the dipole-dipole, dipole-quadrupole, dipole-octupole, quarupole-quadrupole, quadrupole-octupole interactions, and the contribution of the polarization part of the potential. In the ATC method, the parameters δ and γ were calculated as

$$\gamma + i\delta = \frac{nv}{c} \sum_{J_2} \rho_{J_2} (\mathrm{Re}\, \sigma_{J_2} + i\, \mathrm{Im}\, \sigma_{J_2}), \qquad (4)$$

where ρ_{J_2} is the statistical weight of the RV level J_2 of a buffer molecule; $n = 2.47207 \cdot 10^{19}$ is the number of molecules in $1\,cm^3$ at the pressure of 1 atm and the temperature of 296 K; v is the mean thermal velocity of colliding molecules ($v = 8.3447 \cdot 10^4$ cm/s), and

$$\sigma_{J_2} = b_c^2/2 + \int_{b_c}^{\infty} bS(b)\mathrm{d}b\,. \qquad (5)$$

The equations for calculation of different contributions in the interruption function $S(b) = S_1(b) + S_2(b)$ are given in Ref. 2; b is the impact parameter. The parameter $b_c = \mathrm{Sup}\,\{b_0, b_{min}\}$, $b_{min} = 2.71$ Å, and b_0 was calculated from the equation

$$\mathrm{Re}\, S_2(b_0) + |\, \mathrm{Im}\, S_1(b_0)\, | = 1 \qquad (6)$$

(German and Tipping modification, see Ref. 2). Equations (4)–(6) are valid for a particular transition $(i) \to (f)$. The integral in Eq. (5) was calculated numerically.

In the more complicated Robert–Bonamy method,[13] to calculate σ_{J_2}, double integration over the impact parameter b and the velocity of colliding particles v with allowance for the velocity distribution function of molecules $F(v)$ is needed. In the designations of Ref. 2, the equation for σ_{J_2} has the form

$$\sigma_{J_2} = \int_0^{\infty} b\mathrm{d}b \int_0^{\infty} v\mathrm{d}v F(v)[1 - (1 - S_2^{\text{middle}'}) \times$$

$$\times \exp(-S_1 - S_{2,i}^{\text{outer}} - S_{2,f}^{\text{outer}*} - S_2^{\text{middle}''})].$$

In this method, the contributions from the atom-atom potential and distortion of the trajectory of colliding particles are ignored.

For the diagonal matrix element $\mu(V, J, K_a, K_c)$ of the effective dipole moment operator in the basis of RV wave functions, we used the approximation $\mu(V, J, K_a, K_c) = \mu(V, J, K_a) = \mu(V, J, K)$ (that is, the part of the effective dipole moment, being diagonal in the basis of symmetric top rotational wave functions), and the function $\mu(V, J, K)$ was represented by the Pade approximant

$$\mu(V, J, K) = h_0 + \frac{h_1^2}{h_1 - h_2}, \qquad (7)$$

in which

$$h_0 = h_{000}, \quad h_1 = h_{200}\, J(J+1) + h_{020}\, K^2,$$

$$h_2 = h_{400}\, [J(J+1)]^2 + h_{220}\, J(J+1)\, K^2 + h_{040}\, K^4. \qquad (8)$$

The parameters h_{nmk} in Eq. (8) depend on the vibrational state; their values were borrowed from Ref. 14.

The most complete experimental study of self-broadening and shift coefficients for lines of the $H_2{}^{16}O$ ν_2 band was reported in Ref. 15. Table 2 gives the characteristics obtained from comparison of the calculated and experimental[15] values of shifts δ and halfwidths γ. A total of 981 values for the absorption lines with $J \le 20$ and $K_a \le 10$ were used. Table 2 presents the intervals of deviations of the calculated values from the experimental ones $\Delta = |(d^{exp} - d^{cal})|/d^{exp}$ (%) for

$d \equiv (\delta, \gamma)$, N is the number of lines, for which such a deviation was obtained, N/N_{tot} is the relative number with respect to the total number of lines N_{tot}, for which the experimental value of d is known. The parameters Σ, σ, and χ are determined by the following equations:

$$\Sigma = \sum_i^{N_{tot}} (d_i^{exp} - d_i^{cal})^2;$$

$$\sigma = \{\sum_i^{N_{tot}} (d_i^{exp} - d_i^{cal})^2 / N_{tot}\}^{1/2};$$

$$\chi = \{\sum_i^{N_{tot}} ((d_i^{exp} - d_i^{cal}) / d_i^{exp})^2 / N_{tot}\}^{1/2}.$$

Table 2. Statistics of comparison of calculated and experimental[15] values for shifts δ and halfwidths γ of lines of the $H_2{}^{16}O$ ν_2 band in the H_2O–H_2O system

Δ	δ				γ			
	ATC		RB		ATC		RB	
	N	N/N_{tot}, %	N	N/N_{tot}, %	N	N/N_{tot}, %	N	N/N_{tot}, %
0–10%	128	18.1	139	19.7	13	1.8	505	71.1
10–20%	112	15.8	104	14.7	502	70.7	189	26.6
20–30%	108	15.3	92	13.0	191	26.9	14	2.0
30–50%	106	15.0	120	17.0	3	0.4	1	0.1
≥ 50%	253	35.8	252	35.6	1	0.1	1	0.1
Σ, cm^{-2}/atm^2	0.05		0.05		2.61		0.49	
σ, cm^{-1}/atm	0.0086		0.0087		0.061		0.026	
χ	9.6		8.1		0.18		0.098	
N_{tot}	707				710			

Table 3. Experimental and calculated values of halfwidths (10^{-3} cm^{-1}/atm) for some lines with $\Delta K_a = 3$ for the H_2O ν_2 band in the H_2O–H_2O system

Wavenumber ν, cm^{-1}	Assignment	Experiment[16]	Experiment[15]	Calculation
1805.147	5 3 2 – 5 0 5	460	433	447
1835.894	6 3 3 – 6 0 6	377	430	440
1852.405	5 4 1 – 5 1 4	416	415	429
1856.260	6 4 2 – 6 1 5	361	400	414
1876.633	7 3 4 – 7 0 7	420	419	433
1888.818	8 4 4 – 8 1 7	440	403	416
1904.355	5 3 3 – 4 0 4	511	465	469
1904.762	4 4 1 – 4 1 4	455	410	433
1919.688	9 4 5 – 9 1 8	323	370	387
1925.071	5 4 2 – 5 1 5	445	378	407
1926.727	8 3 5 – 8 0 8	411	406	432
1939.126	9 5 4 – 9 2 7	402	350	373
1946.365	6 3 4 – 5 0 5	452	400	407
1951.130	6 4 3 – 6 1 6	419	347	370
1956.235	4 4 1 – 3 1 2	463	428	434
1959.633	5 5 0 – 5 2 3	417	356	392
1976.199	5 4 2 – 4 1 3	426	432	443
1987.340	4 4 0 – 3 1 3	361	–	423
1993.259	7 3 5 – 6 0 6	417	362	385
1998.924	6 4 3 – 5 1 4	488	413	432
2014.434	7 5 3 – 7 2 5	358	316	337
2020.536	8 4 5 – 8 1 8	346	323	349
2026.603	7 4 4 – 6 1 5	427	398	417
2027.025	5 4 1 – 4 1 4	415	438	439
2043.951	8 3 6 – 7 0 7	388	342	357
2060.484	8 4 5 – 7 1 6	416	371	390
2072.541	6 4 2 – 5 1 5	309	370	403
2090.362	5 5 1 – 4 2 2	366	365	394
2097.368	9 3 7 – 8 0 8	343	309	333
2100.433	9 4 6 – 8 1 7	381	336	359
2105.781	5 5 0 – 4 2 3	459	368	395
2106.347	6 5 2 – 5 2 3	441	377	400
2121.269	7 5 3 – 6 2 4	313	397	423
2124.888	7 4 3 – 6 1 6	315	385	397
2137.224	8 5 4 – 7 2 5	343	396	417
2145.468	10 4 7 – 9 1 8	380	310	330
2152.559	10 3 8 – 9 0 9	360	272	295
2156.565	9 5 5 – 8 2 6	306	368	393
2171.256	7 5 2 – 6 2 5	426	–	376
2181.344	10 5 6 – 9 2 7	308	345	369
2185.212	8 4 4 – 7 1 7	320	389	418
2208.737	11 3 9 – 10 0 10	314	220	258
2212.537	11 5 7 – 10 2 8	318	317	341
2248.031	12 4 9 – 11 1 10	276	236	261

Table 2 demonstrates a rather good quality of description of the experimental data for line halfwidths in the RB method. As to line shifts, the both methods give insufficient quality of description of the experimental data.

Comparison of experimental and calculated values for line halfwidths

The results presented in Table 2 demonstrate a close agreement between the calculated and experimental[15] data for line halfwidths γ: about 98% of the experimental data are reconstructed with the accuracy no worse than 20%. The calculated values of γ can be used to assess the experimental data on γ from other sources. Besides Ref. 15, the experimental and calculated values of γ (about 150 values) for the $H_2{}^{16}O$ ν_2 band are presented in Refs. 16 and 17. Reference 16 presents the data of earlier measurements of γ for purely rotational transitions and the ν_2 band. The agreement between the experimental data on γ from Refs. 15 and 16 is, in general, rather good. However, significant discrepancies are observed for some lines. This mostly concerns the lines $(J\ K_a\ K_c) \rightarrow$ $\rightarrow (J'\ K_a'\ K_c')$, for which $\Delta K_a = |\ K_a - K_a'\ | = 3$.

For comparison, Table 3 summarizes all experimental values for γ from Refs. 15 and 16 for lines with $\Delta K_a = 3$, as well as those calculated in this paper (by the RB method). It is seen from Table 3 that the discrepancies between experimental values for line halfwidths can achieve 25%.

Effect of rotational dependence of dipole moment

The effective dipole moment of a molecule in a given vibrational state is, in the general case, a rotational operator, and its matrix elements in the basis of RV wave functions depend on rotational quantum numbers. We have tested three forms of the dependence $\mu(V, J, K)$, which correspond to different approximations used when deriving the effective dipole moment. In the first approximation, μ is independent of J and K. In this approximation, $\mu(V, J, K) = \mu(V) = h_0$. The second approximation corresponds to the case that the effective dipole moment accounts for the square dependence on the elementary rotational operators (that is, up to J_α^2, $\alpha = x, y, z$). It is the most often used approximation. In this approximation, $\mu(V, J, K) = h_0 + h_1$. The operator h_1 is described by Eq. (8). And, finally, we used the approximation, in which the effective dipole moment is determined accurate to square elementary rotational operators (up to J_α^4) (Ref. 14). To avoid divergence of the power series representation of the effective dipole moment (in this case, in terms of the operator J_z^2), in calculation of the matrix element $\mu(V, J, K)$ we used the Pade approximant (7) with the coefficients h_{nmk} calculated in Ref. 14. Figure 1 shows the dependence of shifts for a group of lines $(J = 20\ \ K_a\ \ K_c = 21 - K_a) \rightarrow$ $\rightarrow (J' = 19\ K_a - 1\ K_c' = 20 - K_a)$ on the quantum number K_a for different forms of $\mu(V, J, K)$. The quantum number K_a corresponds to the operator J_z.

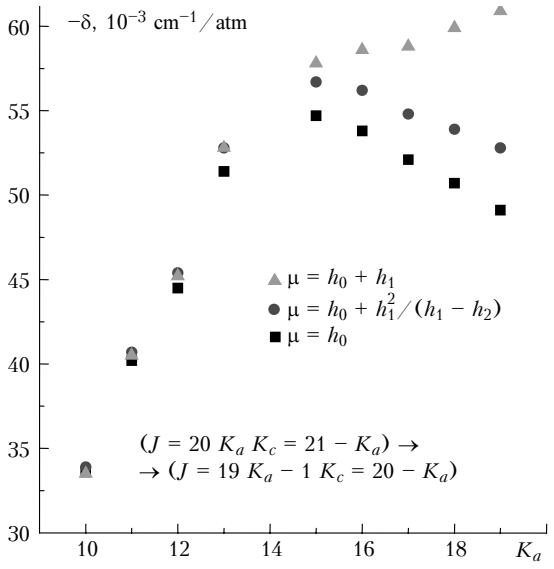

Fig. 1. Dependence of self-pressure induced shift for some lines of the H_2O molecule in the ν_2 band on the quantum number K_a at different representations of the rotational dependence of the effective dipole moment.

It can be seen from Fig. 1 that for the quantum numbers $K_a \le 10$ all forms of $\mu(V, J, K)$ give the same result, and the discrepancy in the values of line shifts appears for $K_a > 10$ (all forms give the same result for line halfwidths at any K_a). The value $K_a = 10$ approximately corresponds to the radius of convergence of the power form of $\mu(V, J, K)$ for the ground and (010) vibrational states.[14] It is seen from Fig. 1 that the largest errors can be obtained when using the second form for $\mu(V, J, K)$. This means that it is better to ignore the rotational dependence of the effective dipole moment when describing shifts of lines with large values of K_a and K_a', than to take into account only the square dependence. Because of divergence of the power representation for the effective dipole moment operator, the last method may give considerable errors in calculated shift coefficients.

Temperature dependence of broadening and shift coefficients

We have calculated the coefficients δ and γ for 981 lines[15] belonging to the ν_2 band of the H_2O molecule in the H_2O–H_2O system at the temperature ranging from 296 to 850 K with the step of 50 K. The results will be presented separately.

Table 4 demonstrates the temperature dependence of two lines, for which we know the experimental values (from Refs. 18 and 19), along with calculations from Ref. 18. Comparison with the experimental data shows that the calculated halfwidths almost coincide with the experimental ones (the experimental temperature dependence of the shift coefficients for these lines is unknown).

Table 4. Temperature dependence of H_2O-H_2O shifts δ and halfwidths γ (10^3 $cm^{-1} \cdot atm^{-1}$) for two lines in the ν_2 band*

Line 1					Line 2				
(7 7 0) → (8 8 1) (ν = 2136.143 cm^{-1})					(8 6 3) → (9 7 2) (ν = 2115.016 cm^{-1})				
T, K	δ_{cal}	γ_{exp}	$\gamma^{1)}{}_{cal}$	γ_{cal}	T, K	δ_{cal}	γ_{exp}	$\gamma^{1)}{}_{cal}$	γ_{cal}
296	−24.8	148±4	–	168	296	−20.3	233±6	–	257
408	−15.3	146±2	131	149	460	−8.5	227±7	191	204
522	−9.5	134±2	122	136	543	−5.4	197±6	176	186
616	−6.5	124±2	116	128	646	−2.9	180±5	160	169
708	−4.4	120±2	110	121	753	−1.3	160±4	147	155
839	−2.6	107±4	103	113	835	−0.5	150±7	139	145

* $\delta_{exp}(T = 296\ K) = -23.6$ for the first line and −20.9 for the second line.[15] The experimental values for γ_{exp} are taken from Ref. 15 for T = 296 K and from Refs. 18 and 19 for other values of the temperature. The calculated values $\gamma^{1)}{}_{cal}$ are taken from Ref. 18.

Conclusion

Our calculations show that the Robert–Bonamy method quite satisfactorily describes experimental data on halfwidths of spectral lines in the ν_2 band of the H_2O molecule in the H_2O–H_2O system, in spite of the fact that the calculations ignored the contribution from the atom-atom potential and trajectory distortion. The comparison with the calculation by the full RB method (see Table 4) shows that these factors are insignificant, at least, for the considered range of rotational quantum numbers. However, there are some problems with calculation of line shifts.

The second conclusion is that the calculations of the parameters δ and γ at large values of the quantum number J (and any K_a) should account for the resonance interactions of vibrational states, including the ground vibrational state. This means that polyads of interacting states should be extended. Besides, for rotational states with large values of the quantum number K_a, asymptotically correct forms should be necessarily used for the effective dipole moment operator. This means that part of the effective dipole moment experimental data on line shift coefficients caused by transitions to the rotational energy levels with large K_a can be used to obtain the information about the form of dependence of the effective dipole moment on rotational operators.

References

1. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Spectroscopy of Water Vapor Molecules* (SB RAS Publishing House, Novosibirsk, 1999), 376 pp.
2. R.P. Leavitt, J. Chem. Phys. **73**, No. 11, 5432–5450 (1980).
3. V.I. Starikov and Vl.G. Tyuterev, Opt. Spektrosk. **88**, No. 5, 761–767 (2000).
4. V.I. Starikov and S.N. Mikhailenko, J. Phys. B **33**, No. 11, 2141–2152 (2000).
5. Vl.G. Tyuterev, V.I. Starikov, and V.I. Tolmachev, Dokl. Akad. Nauk SSSR **297**, No. 2, 345–349 (1987).
6. Vl.G. Tyuterev, J. Mol. Spectrosc. **151**, 130–147 (1992).
7. V.I. Perevalov and Vl.G. Tyuterev, Opt. Spektrosk. **51**, No. 4, 640–649 (1981).
8. V.I. Perevalov and Vl.G. Tyuterev, Opt. Spektrosk. **52**, No. 4, 644–650 (1982).
9. S.N. Mikailenko, Vl.G. Tyuterev, K.A. Keppler, B.P. Winnewisser, M. Winnewisser, G. Mellau, S. Klee, and Narahary K. Rao, J. Mol. Spectrosc. **184**, No. 2, 330–349 (1997).
10. R. Lanquetin, L.H. Coudert, and C. Camy-Peyret, J. Mol. Spectrosc. **195**, No. 1, 54–67 (1999).
11. O.L. Polyansky, J. Tennison, and N.F. Zobov, Spectrochim. Acta, Part A **55**, 659–693 (1999).
12. C.J. Tsao and B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer **2**, No. 1, 41–91 (1962).
13. D. Robert and J. Bonamy, J. de Physic. **40**, No. 10, 923–943 (1979).
14. V.I. Starikov, J. Mol. Spectrosc. **206**, No. 2, 166–171 (2001).
15. R.A. Toth, L.R. Brown, and C. Plymate, J. Quant. Spectrosc. Radiat. Transfer **59**, No. 6, 529–562 (1998).
16. J.P. Mandin, J.M. Flaud, and C. Camy-Peyret, J. Quant. Spectrosc. Radiat. Transfer **23**, No. 4, 351–370 (1980).
17. J.P. Mandin, J.M. Flaud, and C. Camy-Peyret, J. Quant. Spectrosc. Radiat. Transfer **26**, No. 6, 483–494 (1981).
18. B. Labani, J. Bonamy, D. Robert, and J.M. Hartmann, J. Chem. Phys. **87**, No. 5, 2781–2789 (1987).
19. J.M. Hartmann, J. Taine, J. Bonamy, B. Labani, and D. Robert, J. Chem. Phys. **86**, No. 1, 144–156 (1987).