Estimates of rotational constants for $(0V_2 0)$ vibrational states of the H₂O molecule

A.D. Bykov, B.A. Voronin, and S.S. Voronina

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Rotational A, B, C, and centrifugal distortion Δ_k constants for high-excited bending $(0V0)$-type states of the H₂O molecule were derived from *ab initio* calculations of Partridge and Schwenke. Energy levels with $J = 0$, 1, and 2, for $V_2 = 0 \ldots 17$, which are eigenvalues of the 1×1 effective Hamiltonian matrix, were used. Fitting was performed by the least square method; all states were considered as isolated. The rms error did not exceed 0.3 cm⁻¹ for all cases except for the (0 11 0) state. The standard deviation for this case was more than 1 cm⁻¹ that may be explained by the influence of resonance interactions. The exponential equation used earlier reproduced our data satisfactorily for the lower values of V_2. The growth of the A and Δ_k parameters with increasing V_2 does not occur. Above the barrier to linearity, the parameter A becomes stable at the level of 1000 cm⁻¹ and the parameter Δ_k - at the level of 200 cm⁻¹. This can be explained by the effect of strong centrifugal distortion forces at high values of V_2. For the B and C rotational constants, the strong vibrational dependence was not observed.

Introduction

This work is aimed at estimation of the rotational A, B, C, and centrifugal distortion Δ_k constants for high-excited bending vibrational $(0V_2 0)$ states. The estimates obtained from the results of variational calculation of energy levels based on the high-accuracy *ab initio* potential energy function[1] seem to be useful by the following reasons. First, they allow estimation of general regularity in the behavior of these constants of the effective rotational Hamiltonian at high vibrational excitation. Second, these values of the rotational constants can be used as initial values when solving inverse problems and analyzing the role of "dark" states. Third, the constants of high bending vibrational bands are needed for estimation of water vapor absorption in the UV region.

The problem of weak water vapor absorption in the near UV region is well-known (see Ref. 2 and references therein). The analysis shows that the weak H₂O band nearby 0.27 µm cannot be caused by some electronic transition, while rotational-vibrational transitions in this region are believed too weak to cause some marked absorption. (The contribution of HDO absorption in the region of 0.27 µm was estimated in Ref. 3.) A hypothesis about possible intensification of rotational-vibrational (RV) transitions due to the rotational-vibrational-electronic interaction between the ground and excited electronic states was put forward in Ref. 2.

One of the possible explanations to the weak 0.27 µm absorption band may be the rotational-vibrational-electronic interaction between the ground

$\widetilde{X}^1 A_1$ and the excited $\widetilde{B}^1 A_1$ electronic states. It is well-known[4] that if the molecular configuration is close to the linear one, the conic cross section of the potential energy surface of the ground electronic and $\widetilde{B}^1 A_1$ states is observed. The conic cross section is a nonadiabatic effect leading to perturbation of electronic wave functions, namely, their mixing and change in the dipole moments of transitions. Since this effect best shows itself for close-to-linear molecular configurations, to estimate it, we have to know both RV energy levels and off-diagonal Hamiltonian matrix elements calculated with adiabatic wave functions. This interaction can lead to the intensity transfer from the band $\widetilde{B}$ to transitions to high-excited bending vibrational states in the ground electronic state. In this connection, it seems useful to calculate rotational centrifugal constants of high bending states of the $(0V_2 0)$ type. These estimates can be then used to determine the intensity re-distribution between $\widetilde{X}^1 A_1$ and $\widetilde{B}^1 A_1$ bands.

1. Calculation of rotational constants

To obtain the estimates, we used the calculated[1] energy levels with $J = 0$, 1, 2 and $V_2 = 0 \ldots 17$, which are determined as eigenvalues of 1×1 matrices. They are the levels: [000], [101], [111], [110], [212], [211], and [221].

The A, B, C, and Δ_k constants were determined by fitting by the nonlinear least-square method. Since the states considered are high-excited bending states, for which perturbation series diverge for already low values

of the angular momentum quantum number J, the rotational and centrifugal distortion parameters were determined by the equations of the generation function method (see Refs. 5 and 6). In this case, the energy levels were calculated by the following equation:

$$E_{JK\gamma} = E_V + \left(A - \frac{B+C}{2}\right) G(K,\alpha) - \Delta_k G(K,\alpha)^2 +$$
$$+ \frac{B+C}{2} J(J+1) + \delta_{K,1}\gamma \frac{B-C}{4} J(J+1), \quad (1)$$

where

$$G(K,\alpha) = \frac{2}{\alpha} \left(\sqrt{1+\alpha K^2} - 1\right) \quad (2)$$

is the so-called G-function; $\gamma = \pm 1$; $K(= K_a)$ is the rotational quantum number; E_V is the vibrational energy level, all other terms of the series (1) were omitted.

Expansion into the power series in terms of K^2 gives the ordinary Watson representation of the effective rotational Hamiltonian. The initial approximation for the parameters (1) was determined through fitting by the equations:

$$E_{JK_aK_c} = E_V + \left(A - \frac{B+C}{2}\right) K^2 + \frac{B+C}{2} J(J+1) -$$
$$- \Delta_k K^4 + \delta_{K,1}\gamma \frac{B-C}{4} J(J+1). \quad (3)$$

Table 1 presents the vibrational quantum number V_2 determining the vibrational state $(0V_20)$, vibrational energy E_V, rotational A, B, C, and centrifugal distortion Δ_k constants, and parameter α from Eq. (2). The data obtained by fitting to experimental data are given in

parenthesis. The values for the states (000), (010), (020), and (030) were obtained from fitting to the experimental levels from Ref. 7, for (040) − from Ref. 8, for (050) − from Ref. 9, for (060) − from Ref. 10, and for (070) − from Ref. 11. It should be emphasized here that the initial approximations of the rotational and centrifugal distortion constants for the states (060) and (070) in Refs. 10 and 11 were estimated based on the data of Ref. 1. Then they were fitted along with the constants of other vibrational states. The band center for the (070) state was also included in the fitting, and its resulting value changed by almost 125 cm^{-1}. Since only three experimental levels with $K_a = 1$ are now known, for example, for the (070) state (see Ref. 12), the constants are effective because of the small number of energy levels included in the fitting.

The rms deviations of the calculated energy levels do not exceed 0.3 cm^{-1} for all the states but (0 11 0), for which the rms error turns out to be higher than 1 cm^{-1}. So large deviation may be explained by resonance interactions, which were ignored in our calculation (here we used the model of an isolated vibrational state). In particular, it can be the interaction between the levels of 15316.61140 (0 11 0) [1 0 1] and 15327.00870 (0 8 1) [1 1 1], 16037.42210 (1 6 1) [2 0 2] and 16052.99810 (0 11 0) [2 1 2], as well as 16727.00160 (3 4 0) [2 2 1] and 16730.67620 (0 11 0) [2 2 1].

Figure 1 shows the dependence of the A, B, C, and Δ_k constants on the vibrational number V_2. As can be seen from the plots, the rotational B and C constants vary relatively slightly; for example, C decreases from 9.3 to 6.29 cm^{-1} at excitation of 17 vibrational quanta. At the same time, A and Δ_k vary significantly; in particular, Δ_k increases 10000-fold.

Table 1. Rotational A, B, C and centrifugal distortion Δ_k constants (cm^{-1}) of bending $(0V_20)$ vibrational states of the water molecule

| V_2	E_V	A	B	C	Δ_k	α
0	0	27.83(27.88)	14.51(14.52)	9.28(9.27)	0.028(0.032)	0.0036
1	1594	31.13(31.12)	14.66(14.68)	9.14(9.12)	0.048(0.057)	0.0051
2	3151	35.56(35.58)	14.81(14.84)	9.00(8.97)	0.098(0.109)	0.0084
3	4666	42.04(42.13)	14.92(14.97)	8.86(8.83)	0.112(0.244)	0.0147
4	6134	52.63(52.63)	15.01(15.12)	8.74(8.63)	0.924(0.727)	0.0302
5	7542	73.87(51.43)	15.05(15.31)	8.63(8.31)	2.13(5.3)	0.0762
6	8870	130.71(105.7)	15.06(15.35)	8.52(8.38)	6.34(9.3)	0.2135
7	10087(10210)	293.04(127.3)	15.10(15.08)	8.40(8.23)	32.84(7.34)	0.4670
8	11254	532.08	15.50	8.23	161.5	0.6205
9	12533	674.42	16.07	8.04	211.5	0.6387
10	13857	859.71	16.73	7.81	292.2	0.6896
11	15295	960.913	16.19	7.94	328.4	0.6922
12	16824	1031.23	17.56	7.71	361.4	0.7097
13	18424	1043.26	18.26	7.11	364.5	0.7075
14	20310	1051.30	18.63	7.19	368.5	0.7098
15	21915	1086.20	18.69	6.59	369.4	0.6882
16	23549	1096.00	18.68	6.35	324.9	0.5998
17	25464	1215.02	21.38	6.29	421.4	0.7016
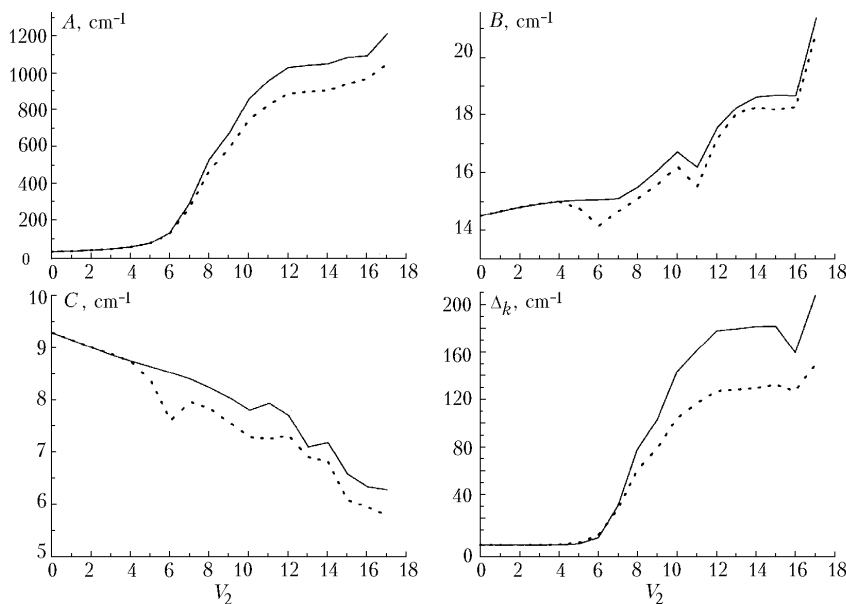
Fig. 1. Dependence of rotational constants of the effective Hamiltonian on the quantum number V_2: the values obtained with the use of G-functions by Eq. (1) (solid curve), the values obtained through fitting by Eq. (3) (dotted curve).

2. Centrifugal stabilization in H$_2$O

It should be noted that for A and Δ_k we did not observe the unlimited exponential growth (see Ref. 5). Starting from $V_2 = 11-12$, the second derivative alternates the sign, and the rate of increase of the rotational constant A for the levels with $V_2 = 11-16$ is similar to the rate of increase for small V_2.

To calculate A and Δ_k, it was proposed in Ref. 5 to use the following equations[13]:

$$A^{(n)} = A^{(0)} + \gamma \exp(a_1 n + a_2 n^2 + a_3 n^3), \qquad (4)$$

where $a_1 = 0.1508959$, $a_2 = 0$, $a_3 = 0.312069 \cdot 10^{-2}$; $\gamma = 2.796889$; $A^{(0)} = 27.885$, $\beta = 0.006$, and n varies from 0 to 17;

$$A^{(n)} = A^{(0)} + \frac{\gamma n}{(1 - \beta n)(1 - \beta(n - 1))} + \dots . \quad (5)$$

The constants in Eqs. (4) and (5) were determined by Starikov from fitting of energy levels up to $V_2 = 4$ inclusive [vibrational state (040)].

Figure 2 depicts the rotational constant A calculated by Eq. (1) (curve *1*), Eq. (3) (curve *2*), Eq. (4) (curve *3*), and Eq. (5) (curve *4*). It is seen that Eq. (4) well describes the behavior of A almost up to the barrier to linearity (for H$_2$O the barrier to linearity is $E_b \sim 11100$ cm^{-1}, $E_{V_2=7} < E_b < E_{V_2=8}$), while Eq. (5) works well only up to $V_2 = 4$. Imperfection of these models can be explained by the fact that few data were used for fitting up to $V_2 = 4$ inclusive.
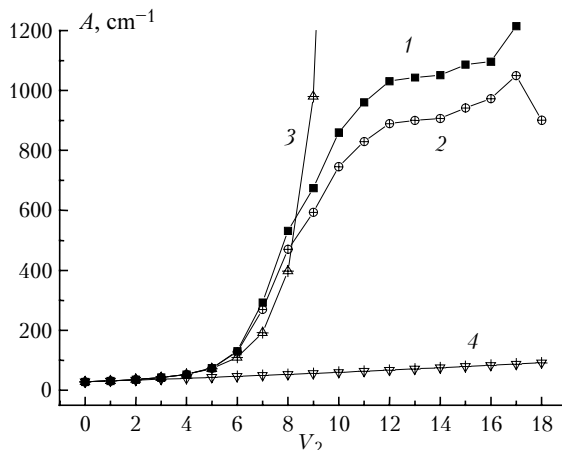

Fig. 2. Rotational constant A calculated by different methods.

The tabulated data are indicative of certain stabilization of the molecular configuration connected with the effect of centrifugal forces. The effective rotational constants can be approximately expressed through the effective moments of inertia − parameters of the effective configuration of the molecule − the mean angle $\langle \theta \rangle$ and the mean bond length $\langle r \rangle$:

$$A^{-1} \sim I_{zz} = \frac{2mM}{m + 2M} \langle r^2 \rangle \langle \cos^2(\theta/2) \rangle ; \qquad (6)$$

$$B^{-1} \sim I_{xx} = 2m \langle \sin^2(\theta/2) \rangle \langle r^2 \rangle , \qquad (7)$$

where m is the mass of the hydrogen atom and M is the mass of the oxygen atom.

Representing then the mean value as

$$\langle \cos^2(\theta/2) \rangle \approx \cos^2(\langle \theta \rangle/2), \quad \langle \sin^2(\theta/2) \rangle \approx \sin^2(\langle \theta \rangle/2), \quad (8)$$

we can introduce the effective values of the angles θ for different vibrational states. Figure 3 shows the values of the effective angle between the bonds for the bending vibrational states of the water molecule. It can be mentioned that excitation of the bending vibration leads to stabilization of the molecular configuration, that is, the angle between the bonds for high-excited states keeps almost unchanged.
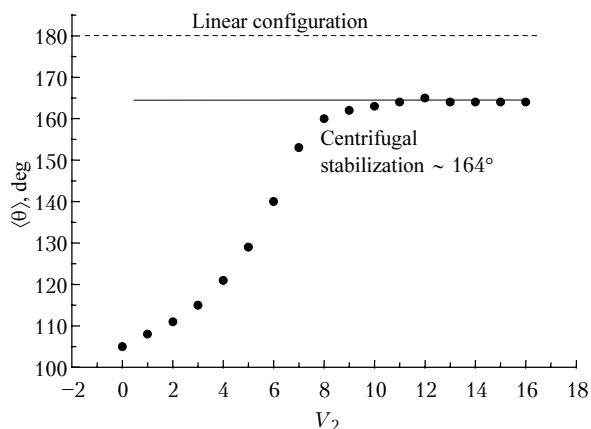

Fig. 3. Dependence of the angle $\langle\theta\rangle$ of the effective configuration of the H_2O molecule on the vibrational quantum number V_2.

Thus, at rather strong excitation, the "mean" molecular configuration stabilizes, that is, the angle between the bonds does not change and equal 180°. This effect is apparently caused by centrifugal forces, which, as the molecule turns around the inertia axis a, "prevent" reaching the linear configuration. The similar effect was found in the calculations[14,15] for the ground vibrational state at high values of the quantum number.
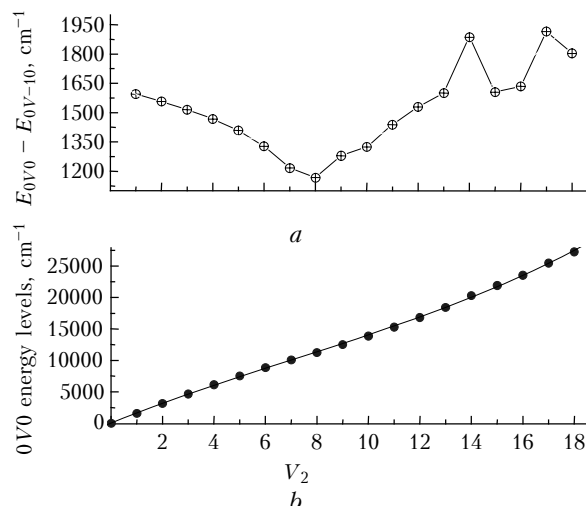

Fig. 4. Dickson effect for energy levels of the bending states of the H_2O molecule.

The following points should be particularly emphasized. Figure 4 depicts the dependence of the differences $E_V - E_{V-1}$ (a) and the vibrational energy E_V (b) on the quantum number V_2. As can be seen

from Fig. 4, at the energy close to the barrier to linearity of the potential function, the character of the dependence changes and the second derivative alternates the sign. As is well-known, triatomic molecules with the low barrier to linearity are characterized by the Dickson effect,[16] which consists in the fact that the difference between the bending vibrational energy levels decreases, when approaching the barrier to linearity, and begins to increase at the energy above the barrier. Interpolation by the cubic polynomial $E = a + b_1V_2 + b_2V_2^2 + b_3V_2^3$ [$a = 48.28$ (115.7), $b_1 = 1648.23(57.2)$, $b_2 = -47.004(7.5)$, $b_3 = 2.227(0.27)$] allows the inflection point to be estimated as $V_{in} = 7.05$, $E_{in} = 10110 \text{ cm}^{-1}$, which agrees with the value of the barrier to linearity $(11105 \pm 5) \text{ cm}^{-1}$ given in Ref. 17.

3. Discussion

We can suggest, as a hypothesis, the idea that the Dickson effect for the $(0V_20)$ vibrational states and the centrifugal stabilization are connected in a certain way. This connection is determined by the change in the properties of bending vibrational states at the energies far exceeding the barrier to linearity.

To describe the dependence of the rotational constant A, we should use the suitable model functions, for example, hyperbolic tangent or arctangent. These functions meet the following conditions: they are monotonically increasing, limited, infinitely differentiable, and have the inflection point. The condition of increase follows from the fact that all the experimental and calculated data available now demonstrate the monotonic increase of A with increasing V_2. The requirement of limitedness follows from the fact that the RV energy cannot be unlimited, because it cannot exceed the molecule dissociation energy. The necessary presence of the point of inflection follows from the form of the calculated dependence.

The fitting for superposition of two hyperbolic tangents was performed for 18 points up to $V_2 = 17$:

$$A = 1501.9 + 444.3\tanh[0.5(x - 8.1)] +$$
$$+ 1025.4\tanh[0.5(x - 19.8)], \qquad (9)$$

where $\tanh(x)$ is the hyperbolic tangent, and the coefficients were determined through fitting by the least square method.

In spite of the fact that deviations of calculation by Eq. (9) from calculation by Eq. (1) reach 70 cm^{-1} for $V_2 = 9$ and the mean deviation is as large as 11 cm^{-1}, the qualitative agreement is observed in the behavior of the functions (Fig. 5).

It should be noted that to extend our knowledge about high-excited states of the water molecule, precision spectral data and accurate calculations both *ab initio* and by the method of effective Hamiltonians are needed.
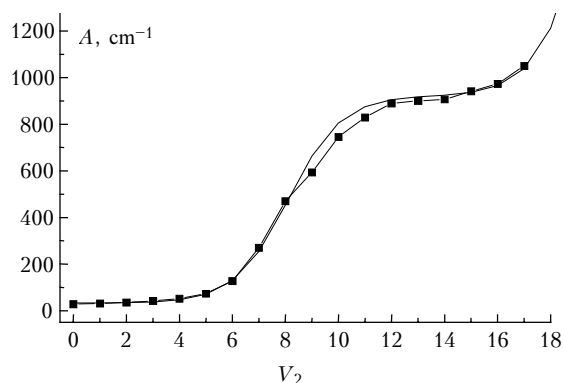
Fig. 5. Extrapolated dependence $A = A(V_2)$: initial values (squares) and values obtained by Eq. (9) (solid line).

Acknowledgments

References

1. H. Partridge and D. Schwenke, J. Chem. Phys. **106**, No. 11, 4618–4639 (1997).
2. M.M. Makogon, Atmos. Oceanic Opt. **14**, No. 9, 696–706 (2001).
3. S.S. Voronina, Atmos. Oceanic Opt. **15**, No. 9, 727–729 (2002).
4. A.J. Varandas, J. Chem. Phys. **107**, No. 3, 867–870 (1997).
5. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Molecular Spectroscopy of Water Vapor* (SB RAS Publishing House, Novosibirsk, 1999), 376 pp.
6. V.I. Starikov, S.A. Tashkun, and Vl.G. Tyuterev, J. Mol. Spectrosc. **151**, No. 1, 130–147 (1992).
7. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *Vibrational-Rotational Spectroscopy of Water Vapor* (Nauka, Novosibirsk, 1989), 296 pp.
8. A.D. Bykov, O.V. Naumenko, L.N. Sinitsa, A.P. Shcherbakov, B. Voronin, and R. Toth, in: *Abstracts of Reports at IV Inter-Republic Symposium on Atmospheric and Ocean Optics*, Tomsk (1997), p. 22.
9. V.I. Starikov and S.N. Mikhailenko, J. Mol. Struct. **449**, 39–51 (1998).
10. B.A. Voronin, A.D. Bykov, O.V. Naumenko, L.N. Sinitsa, and C. Camy-Peyret, in: *Abstracts of Reports at the XXII Meeting on Spectroscopy,* Zvenigorod (2001), p. 165.
11. A.D. Bykov, L.N. Sinitsa, O.V. Naumenko, B. Voronin, C. Camy-Peyret, J.-M. Flaud, and J.-Y. Mandin, SPIE **3583**, 119–124 (1998).
12. Bykov, O. Naumenko, L. Sinitsa, B. Voronin, J.-M. Flaud, C. Camy-Peyret, and R. Lanquetin, J. Mol. Spectrosc. **205**, No. 1, 1–8 (2001).
13. V.I. Starikov and S.N. Mikhailenko, in: *Abstracts of Reports at VIII Joint International Symposium on Atmospheric and Ocean Optics. Atmospheric Physics*, Irkutsk (2001), p. 92.
14. J. Makarewicz, J. Mol. Spectrosc. **130**, No. 2, 316–336 (1988).
15. J. Makarewicz, J. Phys. B. **21**, 3633–3651 (1988).
16. M.S. Child, T. Weston, and J. Tennyson, Mol. Phys. **96**, No. 3, 371–379 (1999).
17. J.S. Kain, O.L. Polyansky, N.F. Zobov, and J. Tennyson, Chem. Phys. Lett. **317**, 365–371 (2000).