CALCULATION OF THE VIBRATIONAL-ROTATIONAL STRUCTURE OF THE SPECTRUM OF WATER FOR THE TEMPERATURE RANGE 300–2500 K

O.K. Voitsekhovskaya

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

Received February 15, 1990

The original set (up to second order inclusively) of derivatives of the dipole moment of H_2O *was determined by solving the inverse electrooptical problem based on the integral intensities, measured experimentally at the normal temperatures, of the vibrational transitions whose wave function incorporates vibrational resonances and anharmonicity. The obtained set was used to extrapolate (to* $T \sim 2500$ K *the integral intensities of the band formed by transitions with high quantum numbers (*$\nu \leq 4$*). The centers and intensities of the vibrational-rotational lines of* H_2O *were calculated and a data base was constructed for the parameters of the spectral lines of* H_2O *for the temperature range* 300–2500 K.

Investigations of water-vapor at high temperatures (~2000 K) involve the problems of propagation of optical radiation in a medium with a nonuniform temperature. At the present time the quantitative analysis of radiation transfer in heated gases is oriented toward using data on the parameters of spectral absorption lines (PSL), formed by vibrational-rotational (VR) transitions.

In this paper a method for calculating the centers and intensities of VR lines of H_2O which contribute to the absorption and emission at temperatures of the medium ~ 2000 K is described. The values obtained for the PSL have been incorporated into a data base, which is one of the information components of an automatic system of high-resolution spectroscopy.[1]

The theoretical analysis is based on a general approach, in which the complete vibrational-rotational Hamiltonian[2] is separated into a group of terms H_{mn} corresponding to the power m of the vibrational (p or q) operators and the power n of the rotational operators (J_α):

$$\begin{aligned} H &= H_{20} + H_{30} + H_{40} + \ldots \text{ (vibrational terms)}, \\ &+ H_{21} + H_{31} + H_{41} + \ldots \text{ (Coriolis terms)}, \qquad (1) \\ &+ H_{02} + H_{21} + H_{22} + \ldots \text{ (rotational terms)}, \end{aligned}$$

This makes it possible to solve the purely vibrational problem with the Hamiltonian

$$H_v = \sum_m H_{m0}. \qquad (2)$$

This means that first the vibrational problem of determining the centers and intensities of the vibrational transitions is solved, and then the rotational structure of the band is resolved and the terms H_{mn} Eq. (1) that are responsible for the vibrational-rotational interactions are taken into account.

USE OF A PHENOMENOLOGICAL VIBRATIONAL HAMILTONIAN FOR DETERMINING THE HAVE FUNCTION OF RESONATING VIBRATIONAL STATES

States with high quantum numbers play the main role in the spectrum of heated gases, and the vibrational resonances must be taken into account in the calculations.

In the water molecule the vibrational resonances connect states with quantum numbers ($V_1 + 1$, $V_2 - 2$, V_3) and (V_1, V_2, V_3), since $2\omega_2 \approx \omega_1$. Resonances in this molecule are classified as cubic and quadratic, depending on the term of the potential function that determines the off-diagonal matrix elements of the Hamiltonian. In this paper, the wave functions of the vibrational resonating states are determined using the effective vibrational Hamiltonian H_V, defined phenomenologically on the subspace of resonating states.[3] In Ref. 3 an empirical set of coefficients of the Hamiltonian, which makes it possible to reconstruct well the experimental energy levels, was found by solving the inverse spectroscopic problem, but the method used to reduce the problem to a block-diagonal form was not discussed.

We checked the extrapolatability of the constants found in Ref. 3 by calculating the energy states with higher vibrational quantum numbers V_1, V_2, and V_3 than those presented in Ref. 3. The values of the energies of these states agreed well with the experimental values (see Table I). This gives a basis for suggesting that the eigenfunctions of H_V

0235-6880/90/06 533-07 $02.00

(Ref. 3) are close to the true eigenfunctions. At the same time, comparing the quantities K_{112} – the cubic anharmonicity constant that follows from the characteristics of the Hamiltonian which were determined – shows that there are significant discrepancies with the known[3] values. For this reason, we used the data of Ref. 3 only to determine the coefficients in the expansion of the wave function of the resonating states, namely, the mixing coefficient C_1

$$\left| V_{res} \right> = \sum_{l}^{n} C_l \left| V_l \right>_0 \tag{3}$$

(n is the number of resonating states).

TABLE I

Comparison of the vibrational energies of H_2O *predicted from the given valves with experiment* (cm^{-1}).

$V_1\ V_2\ V_3$	E_{exp}	E_{calc}	$\Delta E = E_{exp} - E_{calc}$
123	17312.5389	17312.5430	-0.004
500	17458.3540	17458.08925	0.264
401	17495.5284	17495.61138	-0.083
331	18265.8197	18267.8613	-2.04
213	18393.3141	18393.2997	0.014
411	18989.9607	18987.9105	2.05
303	19781.1045	19782.262	-1.15
313	21221.8283	21221.43934	0.389
412	21221.5686	21221.38353	0.185
403	22529.4452	22530.0039	-0.558

DETERMINATION OF THE INTENSITIES OF THE VIBRATIONAL TRANSITIONS OF WATER

The use of a block-diagonal Hamiltonian indicates *a priori* that the transformation $H_V = THT^{-1}$, which reduces the Hamiltonian (2) to a form defined on the subspace of functions coupled by the resonance, is satisfied. But such a transformation corresponds to a change in the wave function $\tilde{\psi}_V = T\psi$, and so as not to lose generality the matrix element of the dipole moment in the basis of the zeroth-order vibrational functions (harmonic oscillator) must be written in the form

$${}_0\left< V_1 V_2 V_3 \right| \tilde{M}_z \left| V'_1 V'_2 V'_3 \right>_0, \tag{4}$$

where

$$\tilde{M}_z = TMT^{-1}. \tag{5}$$

The transformations (4) have been discussed in many works, of which we mention only Refs. 4–11.

A rigorous approach requires that the transformation T in Eq. (5), corresponding to the wave functions (3), be complete:

$$T = e^{-iS_1^v} e^{-iS_2^v} \ldots e^{-iS_n^v} \ldots \tag{6}$$

But, based on the accuracy of the experiment, it Is sufficient to study the twice-transformed dipole moment

$$\tilde{\mu} = \mu_0 + \lambda\{\Delta\mu_1\} + \lambda^2\{\Delta\mu_2\} + O(\lambda^3). \tag{7}$$

The explicit form of the vibrational operator, subjected to a double contact transformation, is presented in Ref. 6 (Appendix XII). Using this form for the transition $\sum |\Delta V_l| \le 2$ we constructed the following general expression for the matrix element of the dipole moment:

$$\left< U_1 U_2 U_3 \right| \tilde{\mu} \left| V_1 V_2 V_3 \right> = \sum_{lk} C_l^{(V)} C_k^{(U)} \left(S_{kl}^1 + S_{kl}^2 + S_{kl}^3 \right). \tag{8}$$

$$S_{kl}^1 = \left[\mu_0 + C\right] \prod_{l=1}^{3} {}_0\left< U_l^k \right| V_l^l \left. \right>_0. \tag{9}$$

$$S_{kl}^2 = \sum_{l \ne \alpha \ne \beta} \left\{ \frac{1}{\sqrt{2}} \mu_l \left[\sqrt{(V_l^l + 1)}\, \delta_{U_l^k V_l^l + 2} + \sqrt{V_l^l}\, \delta_{U_l^k V_l^l - 1} \right] + A_{ll} \left[\sqrt{(V_l^l + 1)(V_l^l + 2)}\, \delta_{U_l^k V_l^l + 2} + \sqrt{V_l^l (V_l^l - 1)}\, \delta_{U_l^k V_l^l - 2} \right] + 2B_{ll} V_l^l \delta_{U_l^k V_l^l} \right\} \times \delta_{U_\alpha^k V_\alpha^l} \delta_{U_\beta^k V_\beta^l}; \tag{10}$$

$$S_{kl}^3 = 2\sum_{l<j} \left\{ A_{lj} \left[\sqrt{(V_l^l + 1)(V_j^l + 1)}\, \delta_{U_l^k V_l^l + 1} \delta_{U_j^k V_j^l + 1} + \sqrt{V_l^l V_j^l}\, \delta_{U_l^k V_l^l + 1} \delta_{U_j^k V_j^l - 1} \right] + B_{lj} \left[\sqrt{(V_l^l + 1) V_j^l} \times \delta_{U_l^k V_l^l + 1} \delta_{U_j^k V_j^l - 1} + \sqrt{V_l^l (V_j^l + 1)}\, \delta_{U_j^k V_j^l + 1} \times \delta_{U_l^k V_l^l - 1} \right] \right\} \times \delta_{U_\gamma^k V_\gamma^l}. \tag{11}$$

where $\delta_{U,V}$ is a δ-function and the indices l and k enumerate the levels in a cluster of resonating states.

The coefficients A_{ij} and B_{ij} have the form

$$A_{ij} = (1/2) \left\{ \mu^{ij} + \frac{3}{2} \left[\sum_{\nu}^{F} \frac{K_{ij\nu}\, \mu_\nu}{\omega_i + \omega_j - \omega_\nu} - \right.\right.$$

$$-\sum_{\nu}^{F}\frac{K_{ij\nu}\,\mu_{\nu}}{\omega_i+\omega_j+\omega_{\nu}}\Bigg]\Bigg\}; \qquad (12)$$

$$B_{ij}=(1/2)\Bigg\{\mu^{ij}-\frac{3}{2}\Bigg[\sum_{\nu}^{F}\frac{K_{ij\nu}\,\mu_{\nu}}{\omega_i+\omega_{\nu}-\omega_j}+$$

$$+\sum_{\nu}^{F}\frac{K_{ij\nu}\,\mu_{\nu}}{\omega_{\nu}+\omega_j-\omega_i}\Bigg]\Bigg\}. \qquad (13)$$

The index F in the summation sign indicates that the summation is not performed over indices corresponding to frequencies connected by a Fermi resonance. The expressions (9)–(11) is in many ways identical to the expression presented in Refs. 8, 9, and 11. The advantage of the form presented above is that it can be used to construct an algorithm for different sets of vibrational quantum numbers characterizing the band.

Thus the expression presented above for the matrix element of the dipole moment take into account both the resonances and centrifugal effects simultaneously.

DETERMINATION OF THE DERIVATIVES OF THE DIPOLE MOMENT OF WATER

There are a large a number of published works on the problem of determining the derivatives of the dipole moment. These works can be classified as follows:

– quantum-mechanical calculations of the derivatives of the dipole moments;

– analysis of a Stark-effect experiment;

and,

– derivation of relations between the matrix element of the dipole moment (MEDM) In the basis of vibrational or vibrational-rotational (VR) wave functions, and the solution of the inverse electrooptic problem, based on an experiment, for the intensities of the bands or separate lines.

The last approach is most often encountered. Some published values of the coefficients in the expansion of the dipole moment (DM) in the normal coordinates are presented in Table II. The data on the coefficients of the DM are obviously very inconsistent. This is explained by the following factors:

a) the diversity of theoretical models, leading to discrepancies in the formulas for the MEDM in terms of the molecular and spectroscopic constants;

b) errors in the experiment on the intensities of lines or vibrational bands (see Table III, where the range of possible values of $S_{V'V}$ of H_2O, established from analysis of the published data, is given); and,

c) use of different sets of values for the remaining molecular constants.

Because of the situation reflected in the data in Tables II and III, in order to perform the calculations correctly a new set of derivatives of the dipole moment, up to and including the second-order derivatives, had to be determined.

It is virtually impossible to determine higher-order derivatives from experiment at this stage with adequate accuracy, since the discrepancy between the experimental values of $S_{V'V}$, for one and the same transition is large.

TABLE II.

The dipole moment of H_2O *(*$D\times10^2$*).*

μ_i^{α}, μ_{ij}^{α}	[17]	[18]	[10]	this paper
μ_1^y	2.81	6.05	-2.16	-2.54
μ_2^y	16.47	-22.27	16.17	16.4
μ_3^x	-8.81	-11.92	9.51	-9.403
μ_{11}^y	1.56	-0.17	-0.17	-0.845
μ_{12}^y	-1.95	-0.335	0.83	-0.505
μ_{13}^x	0.48	0.338	0.70	-0.808
μ_{22}^y	1.31	-1.13	-0.76	1.33
μ_{23}^x	2.16	-2.06	-2.62	-2.17
μ_{33}^y	-0.48	0.25	0.26	-0.288

TABLE III.

Intervals of known valves of $S_{V'V}$ ($\mathrm{cm^{-2}\cdot atm^{-1}}$, $T = 296$ K*) and employed in the analysis of the sets of valves of* $S_{V'V}$.

Band	${S_{v'v}}_{max}$ — ${S_{v'v}}_{min}$	$S_{v'v}$ [14]
ν_1	12.27 — 8.9	12.06
ν_2	317 — 177	257.3
ν_3	196 — 164	171.7
$2\nu_1$	3.02 — 1.13	1.13
$2\nu_2$	1.87 — 1.63	1.898
$2\nu_3$	0.13 — 0.144	0.144
$\nu_1+\nu_2$	0.92 — 0.45	0.921
$\nu_1+\nu_3$	18.5 — 12.0	15.94
$\nu_2+\nu_3$	23.1 — 19.7	19.9
$\nu_3-\nu_2$	$(12.2—6.53)\times10^{-3}$	$6.53\cdot10^{-3}$
$\nu_1-\nu_2$	$(4.7—2.24)\times10^{-3}$	$4.75\cdot10^{-3}$

As one can see from the relations (9)–(11), to calculate the matrix elements of the dipole moment it is necessary to know the force constants $K_{ij\nu}$, the characteristic frequencies, and the coefficients in the expression of the dipole moment.

In our calculations we employed the set of force constants obtained by Claf and presented in Ref. 11, as well as the experimental values of the integrated intensities of the bands from the list in Ref. 14.

In implementing the computational scheme for solving the inverse electrooptic problem we adhered to the method of least squares, as described in Ref. 12. To obtain the simple case of the linear problem, for the initial data in the least-squares equation we substituted the square roots of $\left|\langle V'|M_z|V''\rangle\right|^2$, determined from the experimental values of the integrated intensities.

The choice of signs of the derivatives presented a definite difficulty, since, in this approach, to the N normal vibrations in a molecule there correspond 2^N possible sets of parameters $\{\mu\}$ and additional information must be called upon to chose their optimal values.

After minimization the parameters were chosen from among a set of variants starting from the requirements that the discrepancy between the reconstruction and the predictions of the experimental values of the intensities of the vibrational bands be minimum and that the disagreement with the first derivatives of the dipole moment which were recommended in Ref. 13 be minimum.

Ultimately, with the help of the relations (9)–(11), we found a set of effective derivatives of the dipole moment of H_2O. This set is presented in Table II. It was used as the input information in further extrapolations of the integral intensities of the vibrational transitions of water vapor at high temperatures. Using the computed values of $S_{V'V}$ as the initial data we calculated, using the algorithm of Ref. 15, the centers and intensities of the vibrational-rotational lines of the vibrational bands of the water vapor for forming the corresponding data base in a spectroscopic data retrieval system.[1]

TABLE IV.

Comparison of the intensities of rotational lines of the ν_2 *band of* H_2O *calculated using a rigid-top model and taking into account for the F-factor with experiment* (S = cm^{-2} × atm^{-1}, T = 400 K).

Band	$J''_{\tau'}$ - $J''_{\tau''}$	ν, cm^{-1}	S_{exp} [21]	S_{calc}	δ, %	S^9_{calc} [21]	δ, %
010—000	9_{-1} 10_{-1}	1280.01	0.027	0.0241	11	0.0125	54
010—000	8_2 9_2	1288.89	0.0197	0.0174	12	0.0077	61
010—000	7_{-2} 8_0	1308.21	0.0410	0.0406	1	0.0215	47
010—000	9_{-3} 10_{-3}	1323.35	0.0225	0.0278	23	0.0189	16
010—000	8_{-2} 9_{-2}	1329.9	0.024	0.0218	9	0.014	41
020—010	4_{-1} 5_1	1351.56	0.0051	0.00513	2	—	—
010—000	11_{-7} 12_{-7}	1352.36	0.0096	0.01002	4	0.01	4
020—010	2_1 3_3	1408.52	0.0175	0.0137	21	—	—
010—000	12_{-7} 11_{-7}	1901.82	0.031	0.0349	12.5	0.039	25
010—000	12_{-5} 11_{-5}	1957.69	0.0093	0.0125	34	0.0172	84
010—000	8_{-2} 7_{-4}	1961.19	0.0191	0.0176	8	0.0445	133
010—000	9_0 8_0	2007.74	0.0163	0.0175	7	0.056	243

To calculate the centers of the lines we used sets of experimental values of the energy levels, since the most commonly used form of the effective rotational Hamiltonian, proposed by Watson, has no predictive capability and attempts to extend the calculation of the energies of the VR levels to higher quantum numbers lead to significant errors. The line intensities for a sequence of bands at 6.3 μm $\left(\sum_i \Delta V_i = 1\right)$ were calculated taking into account the F-factor,[1] and the data on the purely rotational spectra and the 2.7 μm band were calculated for the rigid-top model.

In the future we plan to take into account the intramolecular interactions in the regions enumerated, but the technical difficulties, primarily the significant amount of BÉSM-6 processor time required in order to take into account the resonance effects in the intensities of the VR lines, are still insurmountable. Our investigations show[16] that in the case of the calculation of the wide-band spectral characteristics the resonance effects compensate one another.

ANALYSIS OF THE RELIABILITY OF THE COMPUTED PARAMETERS OF THE SPECTRAL LINES OF HEATED WATER VAPOR

Experiments in which the parameters of separate vibrational-rotational lines of high-temperature water vapor are measured involve significant difficulties, stemming in particular, from the fact that the superposition of a large number of lines must be taken into account. For this reason not many investigations of separate VR transitions at $T \simeq 300$ K have been performed.[19–21] In Ref. 19 the transmission functions (I/I_0) were measured at frequencies corresponding to separate VR transitions at $T = 1200$ K. However the unknown instrumental function of the apparatus, in practice, makes it impossible to make a correct comparison with calculations of the PSL. The intensities of several lines of the fundamental bands ν_1 and ν_3 at temperatures of 673, 1273, and 1630 K were measured by C.Y. Maclay,[20] but he was not able to separate the absorption due to separate VR transitions. This result follows from the discrepancy, which exceeds 40%, in the values of the intensities of the same lines referred to $T \sim 296$ K.

The experimental values of the intensities of individual lines of the ν_2 band at $T \sim 400$ K and the results of our calculations are presented in Table IV. The data in Table IV confirm that the vibrational-rotational interactions play a significant role in the Intensities of the lines in bands associated with the bending vibration ν_2.

$$^{\bullet}\delta,\ \% = \left| \frac{S_{\mathrm{exp}} - S_{\mathrm{calc}}}{S_{\mathrm{exp}}} \right| \times 100\ \%$$

CONCLUSIONS

Measurements of the line intensities at high temperatures are performed primarily in the fundamental bands ν_1, ν_2, and ν_3, which are also studied experimentally at normal temperatures, and there is no foundation for concluding from analysis of their values that the methods developed are valid.

There are virtually data on the VR lines of the overtones and combination and difference bands. For this reason the reliability of the PSL data base constructed requires an additional analysis. This analysis was performed in Ref. 16.

I am deeply grateful to N.N. Trifonova and A.V. Fil'chakov for assisting in this work.

REFERENCES

1. O.K. Voitsekhovskaya. N.N. Trifonova, and A. V. Rozina, *Information System for High- Resolution Spectroscopy* [in Russian], Nauka, Novosibirsk (1988), 150 pp.
2. M.R. Aliev and J.C.G. Watson, J. Mol. Spectr. **62**, No. 1, 29–52 (1976).
3. A.D. Bukov, Yu.S. Makushkin, and O.N. Ulenikov, J. Mol. Spectr. **99**, No. 20, 221–227 (1983).
4. D. Papousek and M.R. Aliev, *Molecular Vibrational-Rotational Spectra*, Academia, Pragua (1982).
5. G. Amat, H.H. Nielsen, and G. Tarrago, *Rotation- Vibration Spectra of Polyatomic Molecules*, M. Dekker, New York (1971), 519 pp.
6. Yu.S. Makushkin and V.G. Tyuterev, *Perturbation and Effective-Hamiltonians Methods in Molecular Spectroscory* [in Russian), Nauka, Novosibirsk (1984).
7. D. Berckmans, H.P. Figeys, and P. Geerlings, J. Molec. Struct. (Theochem) **148**, 81–100 (1986).
8. C. Secroun, A. Barbe, and P. Jouve, J. Mol. Spectr. **45**, No. 1, 1–9 (1973)
9. S.J. Yao and J. Overend, *Spectrochim Acta*, **32A**, No. 5, 1059–1066 (1976).
10. Y. Yamaoka and K. Machida, J. Mol. Spectr. **190**, No. 2, 234–244 (1983).
11. J.M. Flaud and C. Cauay-Peyret, *Etude Vibrorotationnelle de la Molecule* H_2O, Author's Abstract of Doctorate of Sci. Phys. (1975).
12. D.L. Albritton, A.L. Schmeltekopf, and R.N. Zare, *Molecular Spectroscopy. Modern Research*, Acad. Press. , New York **11**, Ch. 1, 1–67 (1976);
13. J.M. Flaud and C. Camy-Peyret, *Molecular Spectroscopy, Modern Research*. Acad. Press., New York **11**1 (1985).
14. A. Chedin, M. Hussen, N.A. Scott, Cohen-Hallaleh, and A. Berrior, The GEISA Data Bank: 1984 Version, Laboratoric de Meteorol. Dynamique du C.N.R.S. (1985–1986).
15. O.K. Voitsekhovskaya, Yu.S. Makushkin, N.N. Trifonova, and V.N. Cherepanov, *"Program for calculating vibrational-rotational, line centers and intensities for asymmetric-top molecules"*, COSFAP, No. 004348 (1980).
16. O.K. Voitsekhovskaya. N.N. Trifonova, and N.V. Kuzmina, Opt. Atmos. **3**, No. 5, 485–493 (1990).
17. S.P. Gavva, Candidates Dissertation in Physical Mathematical Sciences, Saratov Polytechnical Institute, Saratov (1984).
18. W.C. Ermler and B.J. Krohn, J. Chem. Phys. **67**, 1360–1370 (1977).
19. A.S. Pine et al., J. Chem. Phys. **12**, No. 1, 413–465 (1965).
20. C.Y. Maclay, J. Chem. Phys. **43**, No. 1. 185–191 (1965).
21. Ben Aryeh, J. Quant. Spectrosc. Rad. Transf. **7**, 211–224 (1967).
22. C. Camy-Peyret et al., J. Mol. Spectr. **110**, 208–228 (1985).