

Rotational Spectrum of the H_2^{16}O Molecule in the (010) Excited Vibrational State

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Five new MW lines of the pure rotational spectrum of water vapor in the (010) excited state have been measured. The analysis of the available data on the (010) vibrational state has been carried out using either a conventional model or a one-dimensional Borel approximation of a Watson-type Hamiltonian.

In both cases a model with 24 parameters up to J^3 was used. The use of the Borel-approximated Watson Hamiltonian resulted in a fit of the experimental data within experimental uncertainty, whereas the fit using the conventional model produced a standard deviation 60 times worse.

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Investigation of the H_2^{16}O rotational spectrum in the first excited state (010) is interesting both for astronomical applications and for the development of the vibration-rotation theory in the case of light molecules. In this paper we present the results of our measurements of five submillimeter-wave lines belonging to the pure rotational spectrum of H_2^{16}O in its excited (010) vibrational state, as well as the results of a combined analysis of the available MW and IR data concerning this state using a one-dimensional approximation of the rotational Hamiltonian.

Up to now, only six lines of the pure rotational spectrum in the (010) vibrational state of water have been measured in the centimeter- and millimeter-wave regions (up to 120 GHz with an experimental uncertainty of about 30–100 kHz) (1–3). The frequency of the strongest line $1_{10} \leftarrow 1_{01}$ in the submillimeter-wave region was measured in Ref. (4). Moreover, in the far-IR region 14 resolved line frequencies of the pure rotational spectrum of water in the (010) state were measured with an accuracy of about 30 MHz (5). In addition, the values of about 340 rotational energy levels of the (010) state with very high rotational quantum numbers (J up to 30 and K up to 14) were derived from the analysis of flame spectra (6).

MEASUREMENTS

We have measured five lines of the pure rotational spectrum of water vapor in the (010) state between 230 and 600 GHz using our submillimeter-microwave RAD spectrometer (7). Because of their very low intensities, the lines $5_{24} \leftarrow 4_{31}$, $6_{34} \leftarrow 5_{41}$, and $4_{22} \leftarrow 3_{31}$ were measured only for a pressure of 1 Torr and the influence of the pressure shift on the frequency of the line could not be evaluated. However, an estimation shows that the shift parameter for this type of line should not exceed 1 MHz/Torr,

and this allows an average accuracy of 1 MHz to these lines. The frequency of the transition $5_{23} \leftarrow 6_{16}$ was measured under a pressure of 0.2 Torr, corresponding to an accuracy of 200 kHz. The values of the five measured frequencies are given in Table I.

ANALYSIS

The effects of centrifugal distortion on the spectrum of the water molecule are rather large, especially in the (010) vibrational state. This can be seen when looking at the ratio of the values of H_k and L_k for the (010) state of water obtained in Ref. (3): this ratio is less than 100 and consequently, for rotational quantum numbers $K \geq 10$, the octic terms make a greater contribution to the rotational energy values than the sextic ones, i.e., the perturbation expansion for these quantum numbers is divergent. Because of this divergence observed in the two published analyses (3, 8) of the data concerning the (010) state of the water molecule, it was necessary to introduce terms up to J_z^{14} in the Watson-type Hamiltonian (9). Moreover, the energy levels with very high rotational quantum numbers were not included in the two fits (3, 8).

TABLE I
MW and Far-IR Line Frequencies of the Pure Rotational Spectrum of H_2^{16}O
in the (010) Vibrational State (in MHz)

Transition $J' K'_A K'_C \leftarrow J'' K''_A K''_C$		$\nu_{\text{exp.}}$	$\nu_{\text{exp.}} - \nu_{\text{cal.}}$
4 2 2	5 1 5	2159.98(10)	-0.079
4 2 3	3 3 0	12008.80(10)	0.317
5 3 2	4 4 1	26834.27(10)	0.095
4 1 4	3 2 1	67803.96(10)	-0.076
4 4 0	5 3 3	96261.16(10)	0.260
2 2 0	3 1 3	119995.94(10)	0.025
5 5 0	6 4 3	232686.70(5)*	0.056
5 2 3	6 1 6	336227.62(20)*	0.148
4 2 2	3 3 1	463169.2(10)*	-0.700
5 2 4	4 3 1	546690.6(10)*	-0.865
6 3 4	5 4 1	595079.8(10)*	0.343
1 1 0	1 0 1	658006.55(5)	0.179
3 2 1	2 1 2	4265389.(30)	101.
8 1 8	7 0 7	4707466.(30)	-3.
3 3 0	2 2 1	4955856.(30)	-62.
4 3 2	3 2 1	5560573.(30)	-46.
6 3 4	5 2 3	6527764.(30)	-55.
4 4 1	3 3 0	6654882.(30)	-64.
4 4 0	3 3 1	6660377.(30)	-79.
5 3 2	4 2 3	6669673.(30)	-98.
5 4 1	4 3 2	7406308.(30)	-5.
6 4 3	5 3 2	8030959.(30)	-113.
7 4 4	6 3 3	8601653.(30)	80.
7 4 3	6 3 4	9006600.(30)	27.
6 5 2	5 4 1	9023625.(30)	69.
7 5 2	6 4 3	9766814.(30)	70.

* Lines measured in this work.

In a previous work (10) we have proposed to use a one-dimensional approximation of the rotational Watson's Hamiltonian, which gives convergent expressions, obtained by rearranging the terms appearing in the divergent expansions. This method has been used to reproduce the data concerning the (010) vibrational state of water and proved to be very useful since it was necessary to introduce in the calculations terms with smaller power in the angular momentum components than in the previous fits (3, 8). In fact the Borel variant¹ of the one-dimensional approximation was used with 24 parameters corresponding to terms up to J^8 (Eq. (1)).

$$\begin{aligned}
 H &= {}^B H_{\text{diag}}^{(8)} + \frac{1}{2} {}^P H_{\text{off-diag}}^{(8)} (J_x^2 - J_y^2) + \frac{1}{2} (J_x^2 - J_y^2) {}^P H_{\text{off-diag}}^{(8)}; \\
 {}^B H_{\text{diag}}^{(8)} &= \int_0^\infty e^{-x} \cdot \frac{u_0^2 u_2 - u_1^2 u_0 + (2u_0 u_1 u_2 - u_0^2 u_3 - u_1^3) x}{u_0 u_2 - u_1^2 + (u_2 u_1 - u_0 u_3) x + (u_1 u_3 - u_2^2) x^2} dx; \\
 {}^P H_{\text{off-diag}}^{(8)} &= b_0 + \frac{b_1(b_0 b_2 - b_1^2) - b_0(b_3 b_1 - b_2^2)}{b_0 b_2 - b_1^2 + b_2 b_1 - b_0 b_3 + b_1 b_3 - b_2^2}; \\
 u_n &= C_n / n! \\
 C_0 &= \frac{B+C}{2} J^2 + \left(A - \frac{B+C}{2} \right) J_z^2; \\
 C_1 &= -\Delta_J J^4 - \Delta_{JK} J^2 J_z^2 - \Delta_K J_z^4; \\
 C_2 &= H_J J^6 + H_{JK} J^4 J_z^2 + H_{KJ} J^2 J_z^4 + H_K J_z^6; \\
 C_3 &= L_J J^8 + L_{JK} J^6 J_z^2 + L_{JK} J^4 J_z^4 + L_{KKJ} J^2 J_z^6 + L_K J_z^8; \\
 b_0 &= \frac{B-C}{2}; \quad b_1 = -2(\delta_J J^2 + \delta_K J_z^2); \\
 b_2 &= 2(h_J J^4 + h_{JK} J^2 J_z^2 + h_K J_z^4); \\
 b_3 &= 2(l_J J^6 + l_{JK} J^4 J_z^2 + l_{KJ} J^2 J_z^4 + l_K J_z^6).
 \end{aligned} \tag{1}$$

The off-diagonal part of the Hamiltonian is usually less divergent than the diagonal one, so we used a Padé approximant for this part. The data were reproduced using this Hamiltonian and in the final fit the data were weighted as follows:

1. For all the pure rotational lines, weights reciprocal to the experimental uncertainty were used (see Table I).

2. Infrared data from Ref. (6) up to $J, K = 14$ were included in the fit with weights of about 1 GHz.

¹ The preliminary attempt to calculate various energy levels in both ground and (010) states of the water molecule on the basis of generalized Euler transformation (GET) (12), one of the other possible variants in the framework of the one-dimensional approximation theory, shows that GET has even more rapid convergence than the Borel approximant, as in the case (12) of a more simple Hamiltonian.

TABLE II

Molecular Constants for the (010) Vibrational State of H_2^{16}O (in MHz)

A	933 255.383(68)	$h_J \cdot 10$	0.11188(22)
B	440 319.457(71)	$h_{JK} \cdot 10$	-0.4910(50)
C	273 681.642(65)	h_K	3.5845(47)
Δ_J	41.9956(19)	$L_J \cdot 10^4$	-0.194(32)
Δ_{JK}	-234.761(11)	$L_{JK} \cdot 10^3$	-0.103(48)
Δ_K	1 752.0121(76)	$L_{JK} \cdot 10^2$	-0.581(33)
δ_J	17.407(16)	$L_{KKJ} \cdot 10$	0.3333(94)
δ_K	115.719(24)	L_K	-0.15384(54)
$H_J \cdot 10$	0.21642(53)	$l_J \cdot 10^4$	-0.108(18)
$H_{JK} \cdot 10$	0.6292(58)	$l_{JK} \cdot 10^3$	-0.200(37)
H_{KJ}	-1.765(16)	$l_{KJ} \cdot 10^2$	0.421(33)
H_K	12.6503(10)	$l_K \cdot 10$	-0.790(33)

All these experimental data were fitted with the aid of either our model (1) or a conventional Watson's Hamiltonian, both expanded up to J^8 . Fit in the model (1), including more than 200 combination differences obtained from the work of Guelachvili (11), resulted in a standard deviation which is 60 times less than that in a conventional model. Thus, the standard deviation equals 700 MHz for the energy levels from Ref. (6), and the maximum difference between experimental and calculated energy levels equals 0.1 cm^{-1} . The experimental and calculated line frequencies of the pure rotational spectrum of the water molecule in the (010) vibrational state are presented in Table I.

In Table II the values of the parameters appearing in our model and derived from the fit are given. These parameters are nearly equal to the ones obtained in Ref. (3), but differ from the parameters of Ref. (8). This is because the fit of the data only up to $J = 9$ (3) does not distort the constants of the conventional Hamiltonian, whereas the fit of the data up to $K = 13$ (8) distorts their values in some way. Because of the good convergence of our Hamiltonian (1), the fit of the data up to $K = 14$ does not distort the constants and consequently we think they have a physical meaning.

Thus, one can draw the following conclusion: in order to obtain both a good accuracy in the fit and "true" values for the constants, the procedure of the one-dimensional approximation of the Watson's Hamiltonian should be used when analyzing experimental data of light molecules with quantum numbers larger than the convergence radius of the conventional Hamiltonian.

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