

The Interacting States (020), (100), and (001) of H₂¹⁷O and H₂¹⁸O

C. CAMY-PEYRET AND J.-M. FLAUD

*Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, CNRS,
Bâtiment 221, Campus d'Orsay, Orsay Cedex 91405, France*

AND

R. A. TOTH

NASA Headquarters, Washington, D. C. 20546

A fit of about 350 rotational levels of the (020), (100), and (001) vibrational states has been performed for H₂¹⁷O as well as for H₂¹⁸O leading to the determination of 51 rotational and coupling constants for each isotopic species. The Fermi-type interaction and the two Coriolis-type interactions have been taken into account by appropriate rotation–vibration operators and the *v*-diagonal part of the Hamiltonian is, for each vibrational state, a Watson-type Hamiltonian. The results are very satisfactory since 87% of the experimental levels are reproduced within $15 \times 10^{-3} \text{ cm}^{-1}$.

INTRODUCTION

This paper is a continuation of our effort to understand precisely the vibration–rotation energy levels of water (*I–3*). In particular we report here a study of the triad of interacting states {(020), (100), (001)} of the isotopic species H₂¹⁷O and H₂¹⁸O. This work has two motivations. First, since the resonances affecting the vibrorotational levels are strongly isotopically dependent it is necessary to study the ¹⁷O and ¹⁸O species for their own and this may eventually lead to an improvement of the potential function. Second, since in high-resolution atmospheric spectra many lines of these two isotopic species contribute to the absorption, a good knowledge of energy levels and wavefunctions is necessary to calculate reliable line positions and intensities.

THEORETICAL CONSIDERATIONS

According to the approximate relation $2\omega_2 \simeq \omega_1 \simeq \omega_3$, the vibrational states of water group into polyads of interacting states corresponding to a given value of $2v_1 + v_2 + 2v_3$; between these states the interactions to be considered are:

- the Fermi-type interaction $\langle v_1 v_2 v_3 | H | v_1 - 1 v_2 + 2 v_3 \rangle$,
- the Coriolis-type interactions $\langle v_1 v_2 v_3 | H | v_1 - 1 v_2 v_3 + 1 \rangle$

TABLE I
 Constants for the Triad of Interacting States (020), (100) and (001) of H₂¹⁷O

	(020)	(100)	(001)
E _v	3148.58 ₄₄ ± 0.74	3649.53 ₉₉ ± 0.74	3748.3193 ± 0.0034
A ^v	35.3409 ₁ ± 0.0033	26.9349 ₁ ± 0.0016	26.4819 ₀ ± 0.0012
B ^v	14.8394 ₄ ± 0.0012	14.30515 ₇ ± 0.00082	14.42872 ₂ ± 0.00049
C ^v	8.96025 ₄ ± 0.00083	9.08041 ₅ ± 0.00063	9.11857 ₀ ± 0.00026
Δ _K ^v	0.11062 ₁ ± 0.00011	(0.29066 ₉ ± 0.00073) × 10 ⁻¹	(0.2843 ₆ ± 0.0011) × 10 ⁻¹
Δ _{JK} ^v	(-0.10562 ₇ ± 0.00021) × 10 ⁻¹	(-0.5331 ₀ ± 0.0039) × 10 ⁻²	(-0.5607 ₉ ± 0.0024) × 10 ⁻²
Δ _J ^v	(0.156 ₈ ± 0.016) × 10 ⁻²	(0.1241 ₉ ± 0.0011) × 10 ⁻²	(0.12909 ₂ ± 0.00049) × 10 ⁻²
δ _K ^v	(0.789 ₁ ± 0.016) × 10 ⁻²	(0.1256 ₄ ± 0.0027) × 10 ⁻²	(0.1199 ₅ ± 0.0027) × 10 ⁻²
δ _J ^v	(0.666 ₆ ± 0.012) × 10 ⁻³	(0.5041 ₅ ± 0.0071) × 10 ⁻³	(0.5289 ₅ ± 0.0029) × 10 ⁻³
H _K ^v	(0.1111 ₆ ± 0.0025) × 10 ⁻²	(0.738 ₅ ± 0.014) × 10 ⁻⁴	(0.890 ₇ ± 0.030) × 10 ⁻⁴
H _{KJ} ^v	(-0.654 ₉ ± 0.046) × 10 ⁻⁴	(-0.1402 ₂ ± 0.0093) × 10 ⁻⁴	(-0.1511 ₆ ± 0.0054) × 10 ⁻⁴
H _J ^v	(0.75 ₃ ± 0.16) × 10 ⁻⁶	(0.478 ₆ ± 0.072) × 10 ⁻⁶	(0.522 ₅ ± 0.027) × 10 ⁻⁶
h _K ^v	(0.176 ₇ ± 0.018) × 10 ⁻³	(0.222 ₂ ± 0.014) × 10 ⁻⁴	(0.2126 ₀ ± 0.0060) × 10 ⁻⁴
h _{JK} ^v			(0.39 ₂ ± 0.19) × 10 ⁻⁶
h _J ^v	(0.327 ₃ ± 0.099) × 10 ⁻⁶	(0.241 ₂ ± 0.046) × 10 ⁻⁶	(0.267 ₃ ± 0.014) × 10 ⁻⁶
L _K ^v	(-0.931 ₁ ± 0.035) × 10 ⁻⁵		(-0.209 ₄ ± 0.025) × 10 ⁻⁶
L _K ^v	(-0.133 ₇ ± 0.026) × 10 ⁻⁵		
P _K ^v	0.3077 × 10 ⁻⁷ ^a		

COUPLING CONSTANTS

$$\begin{aligned}
 h_{32} &= 42.660 \pm 4.2 \\
 h'_{32} &= -0.160_5 \pm 0.047 \\
 h_{43} &= -0.30969_0 \pm 0.00070 \\
 h_{42} &= (-0.696_1 \pm 0.040) \times 10^{-1}
 \end{aligned}$$

Note. All the results are given in cm⁻¹. The quoted errors are 2 standard deviations.

^a Fixed to the H₂¹⁶O value taken from Ref. (1).

and $\langle v_1 v_2 v_3 | H | v_1 v_2 - 2 v_3 + 1 \rangle$,

—the Darling–Dennisson-type interaction $\langle v_1 v_2 v_3 | H | v_1 - 2 v_2 v_3 + 2 \rangle$.

In the triad {(020), (100), (001)} considered here, this last interaction does not occur.

The same Hamiltonian matrix as for H₂¹⁶O (1) has been used to calculate the energy levels. We recall that the *v*-diagonal part¹ of this matrix is for each vibrational state a Watson-type Hamiltonian H_{rv} and that the interaction terms retained in the case of this triad are:

$$H_{32} = h_{32} + h'_{32} J_z^2,$$

$$H_{43} = h_{43}(J_x J_z + J_z J_x),$$

$$H_{42} = h_{42}(J_x J_z + J_z J_x).$$

This Hamiltonian matrix has been diagonalized in a symmetry adapted basis (1) providing us with the wavefunction of a level $(v_1 v_2 v_3)(JK_a K_c)$

¹ The shortened notation $|v\rangle$ stands for $|v_1 v_2 v_3\rangle_0$, which is the eigenfunction of the zero-order vibrational Hamiltonian with the correspondence $v = 0$ for (000), 1 for (010), 2 for (020), 3 for (100), 4 for (001) and so on.

TABLE II
 Constants for the Triad of Interacting States (020), (100) and (001) of H₂¹⁸O

	(020)	(100)	(001)
E _v	3142.43 ₃₅ ± 0.49	3646.30 ₆₁ ± 0.49	3741.567 ₃ ± 0.0039
A ^v	35.1197 ₀ ± 0.0031	26.7690 ₆ ± 0.0016	26.3332 ₄ ± 0.0014
B ^v	14.8347 ₂ ± 0.0011	14.30747 ₁ ± 0.00074	14.42773 ₁ ± 0.00051
C ^v	8.94309 ₆ ± 0.00088	9.06104 ₉ ± 0.00063	9.10058 ₈ ± 0.00028
Δ _K ^v	0.10925 ₁ ± 0.00043	(0.28785 ₉ ± 0.00065) × 10 ⁻¹	(0.2814 ₃ ± 0.0013) × 10 ⁻¹
Δ _{JK} ^v	(-0.1049 ₄ ± 0.0011) × 10 ⁻¹	(-0.5314 ₆ ± 0.0038) × 10 ⁻²	(-0.5579 ₁ ± 0.0025) × 10 ⁻²
Δ _J ^v	(0.1542 ₈ ± 0.0014) × 10 ⁻²	(0.12394 ₂ ± 0.00092) × 10 ⁻²	(0.12914 ₅ ± 0.00051) × 10 ⁻²
δ _K ^v	(0.779 ₆ ± 0.018) × 10 ⁻²	(0.1234 ₁ ± 0.0023) × 10 ⁻²	(0.1182 ₄ ± 0.0028) × 10 ⁻²
δ _J ^v	(0.654 ₇ ± 0.010) × 10 ⁻³	(0.5114 ₉ ± 0.0070) × 10 ⁻³	(0.5301 ₁ ± 0.0030) × 10 ⁻³
H _K ^v	(0.1101 ₇ ± 0.0020) × 10 ⁻²	(0.728 ₆ ± 0.013) × 10 ⁻⁴	(0.885 ₉ ± 0.038) × 10 ⁻⁴
H _{KJ} ^v	(-0.650 ₃ ± 0.045) × 10 ⁻⁴	(-0.1412 ₆ ± 0.0099) × 10 ⁻⁴	(-0.15015 ₈ ± 0.0057) × 10 ⁻⁴
H _J ^v	(0.72 ₃ ± 0.12) × 10 ⁻⁶	(0.465 ₉ ± 0.054) × 10 ⁻⁶	(0.5295 ₂ ± 0.028) × 10 ⁻⁶
h _K ^v	(0.175 ₉ ± 0.021) × 10 ⁻³	(0.222 ₄ ± 0.012) × 10 ⁻⁴	(0.2063 ₅ ± 0.0062) × 10 ⁻⁴
h _{KJ} ^v			(0.49 ₂ ± 0.19) × 10 ⁻⁶
h _J ^v	(0.321 ₃ ± 0.080) × 10 ⁻⁶	(0.286 ₇ ± 0.043) × 10 ⁻⁶	(0.270 ₈ ± 0.015) × 10 ⁻⁶
L _K ^v	(-0.934 ₇ ± 0.028) × 10 ⁻⁵		(-0.215 ₀ ± 0.032) × 10 ⁻⁶
t _K ^v	(-0.111 ₂ ± 0.037) × 10 ⁻⁵		
F _K ^v	0.3077 × 10 ^{-7 a}		

COUPLING CONSTANTS

h ₃₂	= 41.4 ₂₀ ± 3.0
h ₄₂ ¹	= -0.137 ₅ ± 0.033
h ₄₃	= -0.29869 ₂ ± 0.00051
h ₄₂	= (-0.713 ₅ ± 0.046) × 10 ⁻¹

Note. All the results are given in cm⁻¹. The quoted errors are 2 standard deviations.

^a Fixed to the H₂¹⁶O value taken from Ref. (1).

$$|v_1 v_2 v_3 J K_a K_c\rangle = \sum_{r=2,3,4} \sum_K C_K^v |v\rangle |JK\gamma\rangle,$$

where the $|JK\gamma\rangle$ are the usual Wang functions.

RESULTS

Using the experimental data of Ref. (4) for the three vibrational states (020), (100), and (001), we performed for each isotopic species a nonlinear least-squares fit which provided us with the rotational and coupling constants quoted in Table I for H₂¹⁷O and in Table II for H₂¹⁸O. The agreement between the calculation and the experiment is quite satisfactory since a statistical analysis of the differences $\delta = |E^{\text{obs}} - E^{\text{calc}}|$ (in cm⁻¹) between the calculated and the observed energy levels gives:

	H ₂ ¹⁷ O (346 levels)	H ₂ ¹⁸ O (352 levels)
$0 \times 10^{-3} < \delta \leq 15 \times 10^{-3}$	87%	87% (of the levels)
$15 \times 10^{-3} < \delta \leq 40 \times 10^{-3}$	10%	11%
$40 \times 10^{-3} < \delta \leq 75 \times 10^{-3}$	3%	2%

TABLE III

Calculated Rotational Energy Levels for the Vibrational States (020), (100), and (001) of H₂¹⁷O

J	K _a	K _c	(020)	%(2)	%(3)	%(4)	(100)	%(2)	%(3)	%(4)	(001)	%(2)	%(3)	%(4)
0	0	0	3144.978	99.3	0.7	0.0	3653.147	0.7	99.3	0.0	3748.319	0.0	0.0	100.0
1	1	0	3145.068	99.3	0.7	0.0	3676.529	0.7	99.3	0.0	3771.863	0.0	0.0	100.0
1	0	1	3145.098	99.3	0.7	0.0	3688.088	0.7	99.3	0.0	3783.403	0.0	0.0	100.0
1	0	0	3145.008	99.3	0.7	0.0	3694.396	0.7	99.3	0.0	3789.203	0.0	0.0	100.0
2	2	0	3145.121	99.3	0.7	0.0	3721.955	0.7	99.3	0.0	3818.516	0.0	0.0	100.0
2	1	1	3145.133	99.3	0.7	0.0	3730.750	0.7	99.3	0.0	3825.754	0.0	0.0	100.0
2	1	0	3145.049	99.3	0.7	0.0	3746.301	0.7	99.3	0.0	3838.457	0.0	0.0	100.0
2	0	2	3145.020	99.3	0.7	0.0	3751.333	0.7	99.3	0.0	3844.516	0.0	0.0	100.0
2	0	1	3145.008	99.3	0.7	0.0	3757.774	0.7	99.3	0.0	3850.933	0.0	0.0	100.0
2	0	0	3145.008	99.3	0.7	0.0	3764.144	0.7	99.3	0.0	3857.816	0.0	0.0	100.0
3	3	0	3145.159	99.3	0.7	0.0	3792.828	0.7	99.3	0.0	3896.925	0.0	0.0	100.0
3	2	1	3145.171	99.3	0.7	0.0	3801.623	0.7	99.3	0.0	3904.163	0.0	0.0	100.0
3	2	0	3145.087	99.3	0.7	0.0	3817.074	0.7	99.3	0.0	3917.466	0.0	0.0	100.0
3	1	2	3145.058	99.3	0.7	0.0	3826.909	0.7	99.3	0.0	3925.704	0.0	0.0	100.0
3	1	1	3145.046	99.3	0.7	0.0	3835.704	0.7	99.3	0.0	3932.942	0.0	0.0	100.0
3	1	0	3145.046	99.3	0.7	0.0	3844.500	0.7	99.3	0.0	3940.180	0.0	0.0	100.0
3	0	3	3145.017	99.3	0.7	0.0	3853.295	0.7	99.3	0.0	3947.418	0.0	0.0	100.0
3	0	2	3145.005	99.3	0.7	0.0	3862.090	0.7	99.3	0.0	3954.656	0.0	0.0	100.0
3	0	1	3145.005	99.3	0.7	0.0	3870.885	0.7	99.3	0.0	3961.894	0.0	0.0	100.0
3	0	0	3145.005	99.3	0.7	0.0	3879.680	0.7	99.3	0.0	3969.132	0.0	0.0	100.0
4	4	0	3145.181	99.3	0.7	0.0	3908.364	0.7	99.3	0.0	3998.241	0.0	0.0	100.0
4	3	1	3145.193	99.3	0.7	0.0	3917.159	0.7	99.3	0.0	4005.479	0.0	0.0	100.0
4	3	0	3145.109	99.3	0.7	0.0	3932.610	0.7	99.3	0.0	4018.782	0.0	0.0	100.0
4	2	2	3145.080	99.3	0.7	0.0	3942.445	0.7	99.3	0.0	4027.020	0.0	0.0	100.0
4	2	1	3145.068	99.3	0.7	0.0	3951.240	0.7	99.3	0.0	4035.258	0.0	0.0	100.0
4	2	0	3145.068	99.3	0.7	0.0	3960.035	0.7	99.3	0.0	4043.496	0.0	0.0	100.0
4	1	3	3145.039	99.3	0.7	0.0	3968.830	0.7	99.3	0.0	4051.734	0.0	0.0	100.0
4	1	2	3145.027	99.3	0.7	0.0	3977.625	0.7	99.3	0.0	4059.972	0.0	0.0	100.0
4	1	1	3145.027	99.3	0.7	0.0	3986.420	0.7	99.3	0.0	4068.210	0.0	0.0	100.0
4	1	0	3145.027	99.3	0.7	0.0	3995.215	0.7	99.3	0.0	4076.448	0.0	0.0	100.0
4	0	4	3145.000	99.3	0.7	0.0	4004.010	0.7	99.3	0.0	4084.686	0.0	0.0	100.0
4	0	3	3145.000	99.3	0.7	0.0	4012.805	0.7	99.3	0.0	4092.924	0.0	0.0	100.0
4	0	2	3145.000	99.3	0.7	0.0	4021.600	0.7	99.3	0.0	4101.162	0.0	0.0	100.0
4	0	1	3145.000	99.3	0.7	0.0	4030.395	0.7	99.3	0.0	4109.400	0.0	0.0	100.0
4	0	0	3145.000	99.3	0.7	0.0	4039.190	0.7	99.3	0.0	4117.638	0.0	0.0	100.0
5	5	0	3145.187	99.3	0.7	0.0	4067.874	0.7	99.3	0.0	4146.747	0.0	0.0	100.0
5	4	1	3145.199	99.3	0.7	0.0	4076.669	0.7	99.3	0.0	4153.985	0.0	0.0	100.0
5	4	0	3145.115	99.3	0.7	0.0	4092.120	0.7	99.3	0.0	4167.288	0.0	0.0	100.0
5	3	2	3145.086	99.3	0.7	0.0	4101.955	0.7	99.3	0.0	4175.526	0.0	0.0	100.0
5	3	1	3145.074	99.3	0.7	0.0	4110.750	0.7	99.3	0.0	4183.764	0.0	0.0	100.0
5	3	0	3145.074	99.3	0.7	0.0	4119.545	0.7	99.3	0.0	4192.002	0.0	0.0	100.0
5	2	3	3145.045	99.3	0.7	0.0	4128.340	0.7	99.3	0.0	4200.240	0.0	0.0	100.0
5	2	2	3145.033	99.3	0.7	0.0	4137.135	0.7	99.3	0.0	4208.478	0.0	0.0	100.0
5	2	1	3145.033	99.3	0.7	0.0	4145.930	0.7	99.3	0.0	4216.716	0.0	0.0	100.0
5	2	0	3145.033	99.3	0.7	0.0	4154.725	0.7	99.3	0.0	4224.954	0.0	0.0	100.0
5	1	4	3145.006	99.3	0.7	0.0	4163.520	0.7	99.3	0.0	4233.192	0.0	0.0	100.0
5	1	3	3145.006	99.3	0.7	0.0	4172.315	0.7	99.3	0.0	4241.430	0.0	0.0	100.0
5	1	2	3145.006	99.3	0.7	0.0	4181.110	0.7	99.3	0.0	4249.668	0.0	0.0	100.0
5	1	1	3145.006	99.3	0.7	0.0	4189.905	0.7	99.3	0.0	4257.906	0.0	0.0	100.0
5	1	0	3145.006	99.3	0.7	0.0	4198.700	0.7	99.3	0.0	4266.144	0.0	0.0	100.0
5	0	5	3145.000	99.3	0.7	0.0	4207.495	0.7	99.3	0.0	4274.382	0.0	0.0	100.0
5	0	4	3145.000	99.3	0.7	0.0	4216.290	0.7	99.3	0.0	4282.620	0.0	0.0	100.0
5	0	3	3145.000	99.3	0.7	0.0	4225.085	0.7	99.3	0.0	4290.858	0.0	0.0	100.0
5	0	2	3145.000	99.3	0.7	0.0	4233.880	0.7	99.3	0.0	4299.096	0.0	0.0	100.0
5	0	1	3145.000	99.3	0.7	0.0	4242.675	0.7	99.3	0.0	4307.334	0.0	0.0	100.0
5	0	0	3145.000	99.3	0.7	0.0	4251.470	0.7	99.3	0.0	4315.572	0.0	0.0	100.0

Note. %(v) is the mixing coefficient of a given level (v₁v₂v₃)[JK_aK_c] on the vibrational state |v> with v = 2 for (020), 3 for (100), and 4 for (001).

TABLE IV

Calculated Rotational Energy Levels for the Vibrational States (020), (100), and (001) of H₂¹⁸O

J	K _a	K _c	(020)	% (2)	% (3)	% (4)	(100)	% (2)	% (3)	% (4)	(001)	% (2)	% (3)	% (4)
0	0	0	3139.051	99.3	0.7	0.0	3649.688	0.7	99.3	0.0	3741.567	0.0	0.0	100.0
1	1	0	3162.820	99.3	0.7	0.0	3687.741	0.7	99.3	0.0	3776.092	0.0	0.0	100.0
1	1	1	3162.858	99.3	0.7	0.0	3690.774	0.7	99.3	0.0	3782.302	0.0	0.0	100.0
2	2	0	3190.209	99.3	0.7	0.0	3717.418	0.7	99.3	0.0	3811.680	0.0	0.0	100.0
2	2	1	3190.247	99.3	0.7	0.0	3720.451	0.7	99.3	0.0	3817.890	0.0	0.0	100.0
2	2	2	3190.285	99.3	0.7	0.0	3723.484	0.7	99.3	0.0	3824.100	0.0	0.0	100.0
3	3	0	3217.634	99.3	0.7	0.0	3750.128	0.7	99.3	0.0	3853.478	0.0	0.0	100.0
3	3	1	3217.672	99.3	0.7	0.0	3753.161	0.7	99.3	0.0	3859.688	0.0	0.0	100.0
3	3	2	3217.710	99.3	0.7	0.0	3756.194	0.7	99.3	0.0	3865.898	0.0	0.0	100.0
3	3	3	3217.748	99.3	0.7	0.0	3759.227	0.7	99.3	0.0	3872.108	0.0	0.0	100.0
4	4	0	3245.087	99.3	0.7	0.0	3785.871	0.7	99.3	0.0	3901.486	0.0	0.0	100.0
4	4	1	3245.125	99.3	0.7	0.0	3788.904	0.7	99.3	0.0	3907.696	0.0	0.0	100.0
4	4	2	3245.163	99.3	0.7	0.0	3791.937	0.7	99.3	0.0	3913.906	0.0	0.0	100.0
4	4	3	3245.201	99.3	0.7	0.0	3794.970	0.7	99.3	0.0	3920.116	0.0	0.0	100.0
4	4	4	3245.239	99.3	0.7	0.0	3798.003	0.7	99.3	0.0	3926.326	0.0	0.0	100.0
5	5	0	3272.536	99.3	0.7	0.0	3824.647	0.7	99.3	0.0	3955.704	0.0	0.0	100.0
5	5	1	3272.574	99.3	0.7	0.0	3827.680	0.7	99.3	0.0	3961.914	0.0	0.0	100.0
5	5	2	3272.612	99.3	0.7	0.0	3830.713	0.7	99.3	0.0	3968.124	0.0	0.0	100.0
5	5	3	3272.650	99.3	0.7	0.0	3833.746	0.7	99.3	0.0	3974.334	0.0	0.0	100.0
5	5	4	3272.688	99.3	0.7	0.0	3836.779	0.7	99.3	0.0	3980.544	0.0	0.0	100.0
5	5	5	3272.726	99.3	0.7	0.0	3839.812	0.7	99.3	0.0	3986.754	0.0	0.0	100.0
6	6	0	3300.033	99.3	0.7	0.0	3865.456	0.7	99.3	0.0	4016.132	0.0	0.0	100.0
6	6	1	3300.071	99.3	0.7	0.0	3868.489	0.7	99.3	0.0	4022.342	0.0	0.0	100.0
6	6	2	3300.109	99.3	0.7	0.0	3871.522	0.7	99.3	0.0	4028.552	0.0	0.0	100.0
6	6	3	3300.147	99.3	0.7	0.0	3874.555	0.7	99.3	0.0	4034.762	0.0	0.0	100.0
6	6	4	3300.185	99.3	0.7	0.0	3877.588	0.7	99.3	0.0	4040.972	0.0	0.0	100.0
6	6	5	3300.223	99.3	0.7	0.0	3880.621	0.7	99.3	0.0	4047.182	0.0	0.0	100.0
6	6	6	3300.261	99.3	0.7	0.0	3883.654	0.7	99.3	0.0	4053.392	0.0	0.0	100.0
7	7	0	3327.560	99.3	0.7	0.0	3909.298	0.7	99.3	0.0	4082.770	0.0	0.0	100.0
7	7	1	3327.598	99.3	0.7	0.0	3912.331	0.7	99.3	0.0	4088.980	0.0	0.0	100.0
7	7	2	3327.636	99.3	0.7	0.0	3915.364	0.7	99.3	0.0	4095.190	0.0	0.0	100.0
7	7	3	3327.674	99.3	0.7	0.0	3918.397	0.7	99.3	0.0	4101.400	0.0	0.0	100.0
7	7	4	3327.712	99.3	0.7	0.0	3921.430	0.7	99.3	0.0	4107.610	0.0	0.0	100.0
7	7	5	3327.750	99.3	0.7	0.0	3924.463	0.7	99.3	0.0	4113.820	0.0	0.0	100.0
7	7	6	3327.788	99.3	0.7	0.0	3927.496	0.7	99.3	0.0	4120.030	0.0	0.0	100.0
7	7	7	3327.826	99.3	0.7	0.0	3930.529	0.7	99.3	0.0	4126.240	0.0	0.0	100.0
8	8	0	3355.067	99.3	0.7	0.0	3955.173	0.7	99.3	0.0	4155.618	0.0	0.0	100.0
8	8	1	3355.105	99.3	0.7	0.0	3958.206	0.7	99.3	0.0	4161.828	0.0	0.0	100.0
8	8	2	3355.143	99.3	0.7	0.0	3961.239	0.7	99.3	0.0	4168.038	0.0	0.0	100.0
8	8	3	3355.181	99.3	0.7	0.0	3964.272	0.7	99.3	0.0	4174.248	0.0	0.0	100.0
8	8	4	3355.219	99.3	0.7	0.0	3967.305	0.7	99.3	0.0	4180.458	0.0	0.0	100.0
8	8	5	3355.257	99.3	0.7	0.0	3970.338	0.7	99.3	0.0	4186.668	0.0	0.0	100.0
8	8	6	3355.295	99.3	0.7	0.0	3973.371	0.7	99.3	0.0	4192.878	0.0	0.0	100.0
8	8	7	3355.333	99.3	0.7	0.0	3976.404	0.7	99.3	0.0	4199.088	0.0	0.0	100.0
8	8	8	3355.371	99.3	0.7	0.0	3979.437	0.7	99.3	0.0	4205.298	0.0	0.0	100.0
9	9	0	3382.664	99.3	0.7	0.0	3999.821	0.7	99.3	0.0	4234.676	0.0	0.0	100.0
9	9	1	3382.702	99.3	0.7	0.0	4002.854	0.7	99.3	0.0	4240.886	0.0	0.0	100.0
9	9	2	3382.740	99.3	0.7	0.0	4005.887	0.7	99.3	0.0	4247.096	0.0	0.0	100.0
9	9	3	3382.778	99.3	0.7	0.0	4008.920	0.7	99.3	0.0	4253.306	0.0	0.0	100.0
9	9	4	3382.816	99.3	0.7	0.0	4011.953	0.7	99.3	0.0	4259.516	0.0	0.0	100.0
9	9	5	3382.854	99.3	0.7	0.0	4014.986	0.7	99.3	0.0	4265.726	0.0	0.0	100.0
9	9	6	3382.892	99.3	0.7	0.0	4018.019	0.7	99.3	0.0	4271.936	0.0	0.0	100.0
9	9	7	3382.930	99.3	0.7	0.0	4021.052	0.7	99.3	0.0	4278.146	0.0	0.0	100.0
9	9	8	3382.968	99.3	0.7	0.0	4024.085	0.7	99.3	0.0	4284.356	0.0	0.0	100.0
9	9	9	3383.006	99.3	0.7	0.0	4027.118	0.7	99.3	0.0	4290.566	0.0	0.0	100.0

Note. $\% (v)$ is the mixing coefficient of a given level ($v_1 v_2 v_3$)[$J K_a K_c$] on the vibrational state $|v\rangle$ with $v = 2$ for (020), 3 for (100), and 4 for (001).

TABLE V

Example of the Evolution of Mixing Coefficients in an Isotopic Substitution

$(v_1 v_2 v_3) [J K_a K_c]$		E^{calc}	% (020)	% (100)	% (001)
(020) [761]	$H_2^{16}O$	4579.002	95.6	4.2	0.3
	$H_2^{17}O$	4563.754	67.1	28.4	4.5
	$H_2^{18}O$	4551.455	96.3	3.4	0.3
(100) [743]	$H_2^{16}O$	4572.425	3.2	80.1	16.7
	$H_2^{17}O$	4565.834	31.9	59.7	8.4
	$H_2^{18}O$	4558.875	2.8	87.4	9.7
(001) [735]	$H_2^{16}O$	4553.280	0.2	16.6	83.1
	$H_2^{17}O$	4544.287	0.1	12.7	87.2
	$H_2^{18}O$	4536.224	0.1	9.9	90.0

Using the constants of Table I and Table II, we computed the energy levels which are given in Table III for $H_2^{17}O$ and in Table IV for $H_2^{18}O$ together with their mixing coefficients defined by

$$\%_v(v) = \sum_K |C_K^v|^2 \quad \text{with} \quad v = \begin{cases} 2 & \text{for (020),} \\ 3 & \text{for (100),} \\ 4 & \text{for (001).} \end{cases}$$

These mixing coefficients are very important since they allow the easy detection of perturbed levels. These tables contain more calculated levels than observed ones because we hope that an extrapolation to higher J or K_a values than what is experimentally available can be reasonably performed and this should facilitate the assignment of new spectra recorded with larger $P \times l$ product.

It is interesting to compare the evolution of the mixing coefficients of perturbed levels as one goes from $H_2^{16}O$ to $H_2^{17}O$ and to $H_2^{18}O$. Indeed, the magnitude of resonance is very sensitive to isotopic substitution. As an example, we have gathered in Table V the mixing coefficients of the three resonating levels (020) [761], (100) [743], (001) [735].

DISCUSSION

The constants obtained in this work for $H_2^{17}O$ and $H_2^{18}O$ compare very well together as well as with those of $H_2^{16}O$ (1). As the oxygen isotopic substitution does not change the equilibrium B value, one can expect, as has been observed, that the B^v values of the three different isotopic species are not changing very much. A relation between the constant h_{43} involved in the Coriolis resonance between (100) and (001) and the coefficient k_{133} appearing in the expansion of the potential function with respect to normal coordinates is given in Ref. (5). If one assumes that this relation, valid up to the second order of approximation, is applicable for water, then one obtains

$$k_{133} = -869 \text{ cm}^{-1} \quad \text{for} \quad \text{H}_2^{16}\text{O},$$

$$k_{133} = -855 \text{ cm}^{-1} \quad \text{for} \quad \text{H}_2^{17}\text{O},$$

$$k_{133} = -839 \text{ cm}^{-1} \quad \text{for} \quad \text{H}_2^{18}\text{O}.$$

The k_{133} value of H₂¹⁸O confirms the value of this constant obtained from the study of the interacting states (110) and (011) (3).

Finally the wavefunctions obtained in this work will be used in the near future to compute the line intensities for the $2\nu_2$, ν_1 and ν_3 bands of H₂¹⁷O and H₂¹⁸O.

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