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The $4\nu_2$ band of H_2^{16}O

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Résumé. — La première observation de la bande $4\nu_2$ de H_2^{16}O est présentée. Dans ce but, un spectre de la vapeur d'eau chauffée a été enregistré entre 5 930 et 6 440 cm^{-1} par spectroscopie de Fourier. Environ 30 raies de la bande $4\nu_2$ ont été attribuées, ce qui conduit à un centre de bande $4\nu_2 = 6\,134,030 \pm 0,012 \text{ cm}^{-1}$. Les constantes rotationnelles de l'état (040) ont été déterminées et une estimation de l'intensité totale de la bande est proposée :

$$S_v(4\nu_2) = 0,189 \times 10^{-22} \text{ cm}^{-1}/\text{molécule} \cdot \text{cm}^{-2} \text{ à } 296 \text{ K}.$$

Abstract. — The first observation of the $4\nu_2$ band of H_2^{16}O is reported. A hot water vapor Fourier transform spectrum between 5 930 and 6 400 cm^{-1} has been used for this purpose. About 30 lines of the $4\nu_2$ band have been assigned leading to the band center $4\nu_2 = 6\,134.030 \pm 0.012 \text{ cm}^{-1}$. Rotational constants for the (040) vibrational state have been determined and an estimation of the total band intensity is :

$$S_v(4\nu_2) = 0.189 \times 10^{-22} \text{ cm}^{-1}/\text{molecule} \cdot \text{cm}^{-2} \text{ at } 296 \text{ K}.$$

1. Introduction. — Very weak vibration-rotation lines of H_2O often appear in long path atmospheric spectra and their positions and intensities have to be known precisely if one is interested by the absorption of other molecular species. The region 5 930-6 440 cm^{-1} analyzed in this work is a fairly transparent window of the atmospheric spectrum lying between two strongly absorbing regions involving the so-called 1.9 μm and 1.4 μm bands of water. Its analysis originally undertaken in order to confirm our calculations of line parameters for the 1.9 μm bands [1] has led to the discovery of weak unclassified lines which we have been able to assign to the $4\nu_2$ band of water. This very weak band had never been observed before although, as far back as in 1948, Mohler and Benedict [2] stated « The third overtone (040) which should fall in the relatively clear region 1.54-1.64 μm will also be sought under these conditions (large amount of H_2O in the absorbing path) ». The results we have obtained from this study on the (040) vibrational state, are very important as far as the large amplitude motion associated with the bending of the water molecule is concerned.

2. Analysis. — We have used a spectrum of heated water vapor ($\theta = 60 \text{ }^\circ\text{C}$, $P \simeq 90 \text{ torr}$, $L = 40 \text{ m}$) recorded on a Fourier transform spectrometer with a resolution of 0.070 cm^{-1} (for more details see ref. [3, 4]). Generally speaking, the H_2O lines appearing between 5 930 and 6 440 cm^{-1} are very weak ($k_v^N < 1 \times 10^{-24} \text{ cm}^{-1}/\text{molecule} \cdot \text{cm}^{-2}$). At the low wave-number edge of this region, the lines belonging to the wing of the $\nu_2 + \nu_3$ band centered at 5 331.269 cm^{-1} , were easily assigned to transitions of type $\text{R}_{2\bar{1}}$ and $\text{R}_{4\bar{3}}$ ⁽¹⁾ since we had in our possession a reliable synthetic spectrum [1]. At the high wavenumber edge a few lines were found to be $\text{P}_{2\bar{1}}$ transitions of the $2\nu_2 + \nu_3$ band centered at 6 871.522 cm^{-1} [5]. Since no hot band was expected to fall in this region, the remaining lines had to belong to the $4\nu_2$ band of water. Let us remark that this band had never been observed before and the value 6 136 cm^{-1} currently quoted in the literature [6, 7] had been estimated through the study of hot bands in flame spectra [8, 9]. We have been able to assign about 30 lines of the $4\nu_2$ band and the list of all the observed lines between 5 930 and 6 440 cm^{-1} with their positions (precision

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⁽¹⁾ The notation $\Delta J_{\Delta K_a \Delta K_c}$ is used.

$v'v$	σ_{calc}	σ_{obs}	$J'K'_a K'_c$	$JK_a K_c$	K'_c	H
70	5937.423	.422	9 7 2	8 5 3	6.77	13
70	5938.160	.161	9 7 3	8 5 4	20.4	33
70	5940.648	.654	12 4 9	11 2 10	2.46	7
80	5946.841	.843	9 0 9	10 1 10	1.26	3
70	5952.498	.502	9 5 4	8 1 7	4.01	7
70	5954.214	.208	12 6 7	11 4 8	1.20	3
70	5957.958	.962	10 7 3	9 5 4	10.6	20
70	5960.255	.258	10 7 4	9 5 5	3.55	7
70	5962.034	.044	9 4 5	8 0 8	1.93	4
70	5963.518	.513	12 2 10	11 0 11	6.00	16
70	5966.146	.145	12 3 10	11 1 11	2.03	6
70	5968.407	.409	8 8 0	7 6 1	6.58	18
70	5968.412		8 8 1	7 6 2	2.19	
80	5970.102	.106	8 1 8	9 0 9	2.44	6
70	5972.517	.523	13 5 9	12 3 10	1.73	6
70	5974.109	.111	7 5 3	6 1 6	1.88	3
70	5975.886	.885	11 7 4	10 5 5	1.50	4
70	5981.794	.794	11 7 5	10 5 6	4.59	11
70	5983.537	.546	13 6 8	12 4 9	1.08	3
80	5985.743	.740	7 0 7	8 1 8	4.03	7
70	5990.124	.127	13 4 10	12 2 11	2.13	7
70	5990.219	.216	12 7 5	11 5 6	1.61	3
80	5990.915	.911	7 1 7	8 0 8	1.39	2
70	5992.391	.420	9 8 1	8 6 2	2.00	15
70	5992.426		9 8 2	8 6 3	6.00	
70	6001.363	.366	10 5 5	9 1 8	5.34	9
70	6001.538	.543	8 6 2	7 2 5	2.25	3
70	6003.153	.155	12 7 6	11 5 7	0.56	2
80	6003.257	.265	6 0 6	7 1 7	1.97	3
80	6011.485	.489	6 1 6	7 0 7	6.23	8
		6015.377				2
70	6015.509	.509	10 8 2	9 6 3	3.60	8
70	6015.642	.642	10 8 3	9 6 4	1.20	3
70	6016.808	.802	13 2 11	12 0 12	0.62	3
80	6017.162	.162	5 1 4	6 2 5	2.00	4
70	6018.063	.065	13 3 11	12 1 12	1.89	6
70	6019.038	.027	9 6 3	8 2 6	0.93	2
80	6019.260	.257	5 0 5	6 1 6	7.45	9
70	6028.787	.780	8 5 4	7 1 7	0.50	2
70	6031.900	.903	14 3 11	13 1 12	0.56	3
80	6032.101	.103	5 1 5	6 0 6	2.70	4
80	6033.884	.882	4 0 4	5 1 5	2.66	3
80	6034.537	.544	3 1 2	4 2 3	2.26	3
70	6037.453	.455	11 8 3	10 6 4	0.56	2
70	6037.939	.936	11 8 4	10 6 5	1.70	5
70	6039.253	.267	10 4 6	9 0 9	1.52	7
70	6039.269		9 9 1	8 7 2	1.17	
70	6039.268		9 9 0	8 7 1	0.39	
70	6042.033	.040	10 6 4	9 2 7	2.33	4
		6043.114				3
80	6047.794	.792	3 0 3	4 1 4	7.14	7
80	6051.677	.677	3 2 1	4 3 2	1.02	3
80	6053.214	.215	4 1 4	5 0 5	8.94	10
		6053.465				2
80	6062.173	.185	2 0 2	3 1 3	1.76	2
70	6063.802	.807	10 9 1	9 7 2	0.97	4
70	6063.806		10 9 2	9 7 3	0.32	
80	6075.429	.426	3 1 3	4 0 4	2.69	2
80	6077.295	.289	6 2 5	7 1 6	2.06	4
80	6078.268	.260	1 0 1	2 1 2	3.12	4
70	6087.525	.522	11 9 3	10 7 4	0.53	2
70	6089.043	.055	9 5 5	8 1 8	0.82	2
80	6099.301	.299	2 1 2	3 0 3	5.46	5
70	6116.217	.217	9 6 4	8 2 7	0.66	3
80	6125.841	.840	4 2 3	5 1 4	2.68	4
		6129.324				3
80	6177.275	.279	1 1 0	1 0 1	2.15	2
80	6198.138	.126	3 1 2	3 0 3	2.52	3
80	6241.674	.670	5 0 5	4 1 4	2.38	2
80	6260.829	.832	3 2 1	3 1 2	2.37	3
80	6272.381	.376	6 1 6	5 0 5	3.40	4
80	6282.654	.642	7 0 7	6 1 6	3.63	4
80	6288.282	.305	7 1 7	6 0 6	1.23	3
80	6288.304		3 2 2	3 1 3	0.78	
80	6300.460	.464	4 2 3	4 1 4	2.20	3
80	6304.028	.028	8 1 8	7 0 7	3.23	5
80	6317.228	.215	9 0 9	8 1 8	2.35	4
		6334.166				3
80	6334.257	.266	6 2 5	6 1 6	1.19	2
100	6363.246	.243	10 1 9	11 3 8		2
100	6385.345	.336	9 2 8	10 4 7		3
90	6394.441	.460	8 2 7	9 3 6		4
100	6400.245	.248	8 0 8	9 2 7		7
		6401.116				3
100	6443.088	.085	7 1 7	8 3 6		11

Table II. — *Calculated and observed rotational levels of the (040) vibrational state*

J K _a K _c	E _{calc} (cm ⁻¹)	E _{obs}	J K _a K _c	E _{calc} (cm ⁻¹)	E _{obs}
0 0 0	6134.030		5 0 5	6466.512	.509
			5 1 5	6478.798	.800
1 0 1	6157.764	.756	5 1 4	6570.073	.074
1 1 1	6194.792		5 2 4	6642.508	
1 1 0	6201.069	.073	5 2 3	6664.668	
			6 0 6	6589.736	.744
2 0 2	6204.451	.463	6 1 6	6597.729	.732
2 1 2	6236.063	.061	6 1 5	6722.456	
2 1 1	6254.857		6 2 5	6781.509	.510
2 2 1	6358.973		6 2 4	6821.370	
2 2 0	6359.716				
			7 0 7	6729.906	.903
3 0 3	6272.633	.630	7 1 7	6734.979	.975
3 1 3	6297.481	.478	7 1 6	6895.672	
3 1 2	6334.900	.897	7 2 6	6941.551	
3 2 2	6430.583				
3 2 1	6434.194	.193	8 0 8	6887.077	
3 3 1	6601.913		8 1 8	6890.271	.275
3 3 0	6601.974		8 1 7	7087.873	
			8 2 7	7121.886	
4 0 4	6360.509	.507	9 0 9	7061.391	.393
4 1 4	6378.562	.563	9 1 9	7063.408	
4 1 3	6440.367		9 1 8	7297.583	
4 2 3	6525.298	.300	9 2 8	7321.818	
4 2 2	6535.585				
4 3 2	6699.256		10 0 10	7252.968	
4 3 1	6699.674		10 1 10	7254.257	

Standard deviation of the fit : 0.006 cm⁻¹.

± 0.005 cm⁻¹) and intensities is given in table I. From the observed transitions and from the ground state energy levels [10] we have deduced the rotational levels of the (040) vibrational state appearing in table II.

As far as the intensities are concerned the behaviour of the 4ν₂ band is very peculiar. Practically, only the P branch appears, whereas the Q and R branches are very weak. Moreover, the intensity of the lines decreases very rapidly when the quantum number K_a increases and it has been impossible to detect lines with K_a ≥ 3. A similar but less pronounced behaviour has already been observed for the 3ν₂ band [3]. On the other band, as in 3ν₂, accidental resonances can occur. This is the case for the level [945] of (040) ⁽²⁾ which is highly perturbed through a Coriolis resonance with the level [919] of (021) [11, 5]. In these conditions, one can observe 4ν₂ lines originating from this perturbed level and lying in the 2ν₂ + ν₃ region.

⁽²⁾ The notation [JK_a K_c] is used for the rotational quantum numbers and (ν₁ ν₂ ν₃) for the vibrational quantum numbers.

Their intensity is enhanced because of the mixing with a vibrational state having a stronger transition moment with the ground state.

3. **Theoretical.** — Although there is a Fermi-type interaction between (040) and (120) it is possible to treat the rotational levels of (040) determined from experiment with the usual Watson-type hamiltonian [12]. The rotational constants obtained through a least squares fit of the experimental energy levels are listed in table III. These constants have been used to calculate levels unobserved in this work but which could be detected when high resolution spectra will be recorded with a higher pressure path length product. One important result of this study is the precise determination of the band center

$$4\nu_2 = 6134.030 \pm 0.012 \text{ cm}^{-1}.$$

Table III. — *Rotational constants of the (040) vibrational state of H₂O.*

	v = (040)
E _v	6134.030 ₀ ± 0.012
A ^v	52.651 ₀₄ ± 0.015
B ^v	15.0611 ₇ ± 0.0063
C ^v	8.6790 ₁ ± 0.0030
Δ _K ^v	0.6794 ₁₃ ± 0.0049
Δ _{JK} ^v	(-0.254 ₉ ± 0.010) × 10 ⁻¹
Δ _J ^v	(0.1578 ₂ ± 0.0098) × 10 ⁻²
δ _K ^v	(0.255 ₅ ± 0.032) × 10 ⁻¹
δ _J ^v	(0.758 ₆ ± 0.042) × 10 ⁻³
H _K ^v	(0.1510 ₂₅ ± 0.0098) × 10 ⁻¹
H _{KJ} ^v	(-0.54 ₄ ± 0.14) × 10 ⁻³
h _K ^v	(0.78 ₉ ± 0.20) × 10 ⁻³

All the results are given in cm⁻¹. The quoted errors are 95% statistical confidence intervals.

This result should be very useful for the improvement of the bending potential function of water. Indeed previous theoretical calculations were unable to predict a satisfactory value for this band center (see for example ref. [13, 14]).

Having in mind possible applications to atmospheric studies we have computed, by the method developed in ref. [3], the complete spectrum of the

◀ Table I. — *List of observed water vapor lines between 5 930 and 6 440 cm⁻¹.*

The meaning of the different columns is :
 — v' v upper and lower vibrational states of the transition with the correspondence 0=(000), 7=(011), 8=(040), 9=(120) and 10=(021).
 — σ_{calc} and σ_{obs} calculated and observed wavenumbers of the line in cm⁻¹.
 — J' K'_a K'_c J K_a K_c rotational quantum numbers of the upper and lower levels.
 — k_c^N computed line intensity in 10⁻²⁵ cm⁻¹/molecule . cm⁻² at 296 K.
 — H percentage of absorption at the center of the line for the heated spectrum.

$4\nu_2$ band ⁽³⁾. Since it is a B-type band the transformed transition moment operator can be expanded as [15] :

$${}^v\mu'_z = {}^v\mu'_1 \varphi_x + {}^v\mu'_5 \{ \varphi_z, iJ_y \} + \dots \quad v = 8 \quad \text{for } (040).$$

Using about 20 measured intensities (relative precision 25 %), we have obtained

$${}^8\mu'_1 = (0.486_4 \pm 0.012) \times 10^{-4} \text{ D}$$

⁽³⁾ This list is available from the authors.

$$\text{and } {}^8\mu'_5 = (0.1177_1 \pm 0.0019) \times 10^{-4} \text{ D.}$$

This leads to a total band intensity (i.e. the sum of the individual line strengths) of

$$S_v(4\nu_2) = 0.189 \times 10^{-22}$$

(in $\text{cm}^{-1}/\text{molecule} \cdot \text{cm}^{-2}$ at 296 K)

with an estimated precision of 25 %.

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