

Hot Bands of Water in the ν_2 Manifold up to $5\nu_2-4\nu_2$

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A spectrum of the hot water molecule has been recorded in emission at a temperature of 1000°C in the region 900 cm^{-1} to 2000 cm^{-1} . A total of 4381 lines were observed; 1750 are assigned, mostly to the ν_2 , $2\nu_2 - \nu_2$, $3\nu_2 - 2\nu_2$, $4\nu_2 - 3\nu_2$, and $5\nu_2 - 4\nu_2$ bands. The $5\nu_2 - 4\nu_2$ band has been seen for the first time and the rotational analysis of the other hot bands has been extended to high J and K_a values. The assignment of transitions involving previously unobserved levels was achieved using high accuracy *ab initio* electronic structure calculations, an *ab initio* adiabatic correction to this potential, and variational nuclear motion calculations of the spectra. The band origin of $5\nu_2$ is determined to be $7542.39 \text{ cm}^{-1} \pm 0.05 \text{ cm}^{-1}$, significantly different from the value obtained from the “dark state” perturbative treatment.

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I. INTRODUCTION

The scientific literature on the vibration–rotation bands of water is vast and the spectra are used in many applications, such as the identification of water vapor in sunspots (1). The subject of this paper is the hot bands of the ν_2 sequence. In classic works by Flaud, Camy-Peyret, and co-authors (2–5), rotational energy levels in the $\nu_2 = 0, 1, 2, 3$, and 4 vibrational states were determined from hot water emission spectra from flames and overtone absorption spectra for the $3\nu_2$ and $4\nu_2$ bands. Most of these levels were used in the comprehensive water vapor atlas (6). Subsequently improved room temperature spectra of ν_2 (7), (8), $2\nu_2 - \nu_2$ (9), and $4\nu_2$ bands (10) (among many other bands) have been observed and assigned. More recently, Dana *et al.* (11, 12) have measured new flame spectra. They concentrated on measuring collisional linewidths, rather than the determination of new energy levels, but they did assign some new rotational lines, particularly for the $4\nu_2 - 3\nu_2$ band. A new bending–rotation effective Hamiltonian analysis of the published $\nu_2 = 0$ and 1 rotational energy levels, based on the modified model due to Makarewicz (13), was carried out by Coudert (14) as well as very recent ν_2 band analysis (15).

Further expansion of the ν_2 manifold of levels up to $5\nu_2$ has been hampered by the extreme weakness of this band (see for example (16, 17)).

Another reason there are problems in assigning the higher K_a rotational levels of highly excited bending vibrational states is that the conventional power series effective rotational Hamiltonian diverges at about $K_a = 15$ for the ground

vibrational state (18) and $K_a = 10$ for the (010) state (19). This trend continues, so divergence can be expected for K_a values near unity for the (040) and (050) states. One way of solving this problem is to substitute variational calculations using a fitted potential energy surface (e.g., (20)) for the conventional effective Hamiltonian approach. The stretching energy levels of water are known up to 25 000 cm^{-1} (21) and have been used for the fitting the effective potential energy surface (PES) (22). In contrast, the highest bending levels known experimentally lie at 7000 cm^{-1} (5). The addition of higher K_a rotational levels of $\nu_2 = 4$ and any levels of $\nu_2 = 5$ would be of great value in any attempt to improve the bending part of the water PES.

The only source of experimental information on the (050) vibrational state until now has been the so-called “dark state” analysis (23). The strong resonance between the (130) and (050) states leads to a shift of the (130) levels because of interactions with (050) levels. Thus information on the value of the (050) energy levels could be indirectly obtained from the known (130) values. The band origin of the (050) state was determined to be 7552 cm^{-1} (23). However, recent theoretical analysis (22), based on the use of variational calculations and spectroscopically determined potential energy surfaces, has suggested that this value is too high by between 10 and 15 cm^{-1} .

The hot band spectra associated with the ν_2 mode of water were recorded a few years ago in an attempt to identify lines in the Kitt Peak sunspot spectra (1), (27), (28). Since these laboratory spectra had a temperature of only 1000°C, they were not useful for this purpose. It was not until spectra were recorded at 1550°C (1), (27) that we obtained a line density in the pure rotational region (400–900 cm^{-1}) that was comparable to the line density in the sunspot. The identification of water vapor in the sunspot (1) was followed by a partial assignment (27) of the 1550°C laboratory spectrum.

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TABLE 1

List of H₂¹⁶O Transitions Assigned to 020–010 Hot Band (Wavenumbers in cm⁻¹, Intensities (Int) in Arbitrary Relative Units)

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1019.84312	.74	12	3	10	13	4	9	1213.86427	1.80	10	4	6	11	5	7
1038.60394	.68	9	1	8	10	4	7	1217.41048	2.42	16	1	16	16	2	15
1042.18830	.81	10	2	9	11	3	8	1217.75920	5.50	10	8	3	11	9	2
1076.85496	.63	8	1	8	9	2	7	1218.63724	2.81	9	5	5	10	6	4
1076.92983	.66	14	5	10	15	6	9	1219.95702	8.36	9	5	4	10	6	5
1101.44909	.25	14	6	9	15	7	8	1225.62010	4.78	9	6	3	10	7	4
1103.90466	1.30	12	4	9	13	5	8	1225.82008	6.79	8	3	6	9	4	5
1108.41637	.67	7	0	7	8	3	6	1226.86696	3.25	16	1	16	17	0	17
1129.87354	.56	15	5	10	16	6	11	1227.40479	6.20	10	9	2	11	10	1
1131.24451	1.70	13	6	7	14	7	8	1228.52932	7.40	9	4	5	10	5	6
1133.86541	2.14	10	3	8	11	4	7	1230.41860	1.34	17	1	16	18	2	17
1144.80547	1.34	12	5	8	13	6	7	1232.07010	9.11	9	7	2	10	8	3
1145.22371	1.57	13	8	5	14	9	6	1240.68926	10.50	8	4	5	9	5	4
1146.47626	.95	11	4	8	12	5	7	1240.88567	3.41	15	0	15	15	1	14
1152.25879	2.49	12	6	7	13	7	6	1242.38084	8.11	9	8	1	10	9	2
1152.31317	1.23	13	9	4	14	10	5	1243.02137	10.83	8	5	4	9	6	3
1153.07286	.77	12	6	6	13	7	7	1246.67548	4.17	15	0	15	16	1	16
1159.02477	.91	12	5	7	13	6	8	1246.83723	2.29	8	4	4	9	5	5
1160.10132	2.48	12	7	6	13	8	5	1248.17728	10.60	8	6	3	9	7	2
1160.25039	.82	12	7	5	13	8	6	1251.83738	.67	15	3	12	16	4	13
1168.19179	1.23	11	5	7	12	6	6	1252.72601	5.68	9	9	0	10	10	1
1169.17464	2.54	12	8	5	13	9	4	1255.16694	1.45	11	10	1	12	11	2
1170.33273	1.23	18	1	18	18	2	17	1256.54657	11.40	8	7	2	9	8	1
1175.84912	3.78	11	6	5	12	7	6	1258.70923	1.09	13	3	10	14	4	11
1176.12705	1.45	11	6	6	12	7	5	1261.92435	3.22	7	3	5	8	4	4
1176.89270	4.03	11	5	6	12	6	7	1263.22823	2.09	15	1	14	16	2	15
1177.19864	1.97	12	9	4	13	10	3	1265.88868	1.53	15	2	13	16	3	14
1182.22722	4.58	10	4	7	11	5	6	1266.43708	5.77	7	4	4	8	5	3
1183.83624	1.28	11	7	5	12	8	4	1266.44687	5.09	14	1	14	15	0	15
1183.88039	3.71	11	7	4	12	8	5	1267.21119	10.34	8	8	1	9	9	0
1187.22071	1.19	18	1	18	19	0	19	1267.40366	5.09	7	5	3	8	6	2
1193.35586	4.02	11	8	3	12	9	4	1267.51310	13.28	7	5	2	8	6	3
1193.90832	1.87	17	0	17	17	1	16	1268.76124	12.72	7	4	3	8	5	4
1193.92952	5.92	10	5	6	11	6	5	1269.25766	6.10	9	3	6	10	4	7
1196.60882	1.42	13	4	9	14	5	10	1272.68272	13.07	7	6	2	8	7	1
1197.55862	1.87	10	5	5	11	6	6	1273.29551	7.21	6	2	5	7	3	4
1198.44028	.86	12	4	8	13	5	9	1276.55334	3.05	8	3	5	9	4	6
1199.98165	5.34	10	6	5	11	7	4	1280.00751	3.42	14	2	13	15	1	14
1202.22980	3.16	11	9	2	12	10	3	1281.23522	15.39	7	7	0	8	8	1
1203.88923	3.64	11	4	7	12	5	8	1283.69849	2.14	14	3	12	15	2	13
1207.03389	2.43	17	0	17	18	1	18	1284.30091	2.04	17	1	16	17	2	15
1207.82600	4.96	10	7	4	11	8	3	1286.12067	7.58	13	0	13	14	1	14
1213.09646	2.57	9	4	6	10	5	5	1286.13974	2.70	13	1	13	14	0	14
								1287.55695	5.60	13	0	13	13	1	12

TABLE 1—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1288.13937	11.08	7	3	4	8	4	5	1340.61956	21.20	4	4	1	5	5	0
1291.34787	15.92	6	4	3	7	5	2	1340.63495	9.02	4	4	0	5	5	1
1291.61027	1.28	14	4	11	15	3	12	1343.97967	3.26	10	1	9	11	2	10
1291.90521	16.80	6	5	2	7	6	1	1344.45732	5.07	10	0	10	11	1	11
1291.93029	6.59	6	5	1	7	6	2	1344.59251	13.34	10	1	10	11	0	11
1292.01132	6.20	6	4	2	7	5	3	1344.72456	4.09	6	2	4	7	3	5
1292.17443	3.00	13	2	11	14	3	12	1346.00350	18.59	4	3	2	5	4	1
1292.82688	13.67	6	3	4	7	4	3	1347.03157	7.51	4	3	1	5	4	2
1296.12649	4.65	13	1	12	14	2	13	1347.46303	8.99	10	2	9	11	1	10
1296.68485	1.64	13	2	12	14	1	13	1351.57013	13.04	4	2	3	5	3	2
1297.13470	15.15	6	6	1	7	7	0	1354.88089	4.92	10	3	8	11	2	9
1297.24605	6.29	6	6	0	7	7	1	1355.20988	12.25	5	2	3	6	3	4
1299.73541	1.00	13	3	11	14	2	12	1356.03843	8.88	10	1	10	10	2	9
1301.87233	2.97	16	2	15	16	3	14	1356.71092	2.01	13	2	12	13	3	11
1304.28566	5.42	6	3	3	7	4	4	1357.20566	3.10	10	0	10	10	1	9
1305.70338	3.41	12	0	12	13	1	13	1358.72196	10.13	9	1	8	10	2	9
1305.73913	9.41	12	1	12	13	0	13	1358.86977	5.98	13	1	12	13	2	11
1310.48580	6.71	12	1	12	12	2	11	1363.56408	13.90	9	0	9	10	1	10
1310.78178	2.37	12	0	12	12	1	11	1363.83407	5.30	9	1	9	10	0	10
1312.41828	2.32	12	1	11	13	2	12	1363.92699	2.06	16	3	14	16	4	13
1313.10348	.58	13	4	10	14	3	11	1365.09467	3.43	9	2	8	10	1	9
1313.22952	5.20	11	2	9	12	3	10	1369.53144	5.19	4	2	2	5	3	3
1313.44169	6.03	12	2	11	13	1	12	1370.57343	3.52	15	2	14	15	3	13
1315.92616	3.79	5	2	4	6	3	3	1370.89231	7.82	3	3	1	4	4	0
1315.99309	7.38	5	4	2	6	5	1	1371.03943	18.74	3	3	0	4	4	1
1316.12958	18.63	5	4	1	6	5	2	1372.24434	3.94	8	1	7	9	2	8
1316.54850	17.58	5	5	0	6	6	0	1375.06671	6.40	12	2	11	12	3	10
1316.79340	3.54	12	3	10	13	2	11	1377.09000	2.12	3	1	3	4	2	2
1319.96385	1.26	15	2	14	15	3	13	1378.33731	3.50	9	1	9	9	2	8
1320.32737	6.52	5	3	3	6	4	2	1378.54180	1.72	9	3	7	10	2	8
1320.60417	3.70	15	1	14	15	2	13	1378.96673	2.54	12	1	11	12	2	10
1320.94723	2.16	10	2	8	11	3	9	1379.41490	1.04	15	3	13	15	4	12
1324.34944	16.53	5	3	2	6	4	3	1380.62376	9.73	9	0	9	9	1	8
1325.15840	11.43	11	0	11	12	1	12	1381.76352	5.83	3	2	2	4	3	1
1325.22712	4.15	11	1	11	12	0	12	1382.42315	6.17	8	0	8	9	1	9
1326.81572	7.17	9	2	7	10	3	8	1382.97001	16.01	8	1	8	9	0	9
1327.73554	4.47	4	1	4	5	2	3	1383.65338	10.67	8	2	7	9	1	8
1328.43917	7.55	11	1	10	12	2	11	1384.17033	11.90	7	1	6	8	2	7
1330.32685	2.59	11	2	10	12	1	11	1385.28945	3.09	15	2	13	15	3	12
1331.79467	3.09	8	2	6	9	3	7	1387.93366	15.32	3	2	1	4	3	2
1333.97236	8.01	11	0	11	11	1	10	1393.10931	3.21	11	2	10	11	3	9
1337.29584	9.69	7	2	5	8	3	6	1394.38103	3.41	14	3	12	14	4	11
1338.28566	5.36	14	2	13	14	3	12	1394.42516	3.28	5	0	5	6	1	6
1339.46400	1.57	14	1	13	14	2	12	1394.54264	3.27	6	1	5	7	2	6

TABLE 1—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1399.96305	9.18	11	1	10	11	2	9	1454.21321	5.77	7	2	6	7	3	5
1400.08700	10.99	8	1	8	8	2	7	1455.22048	2.45	11	4	8	11	5	7
1400.94231	17.31	7	0	7	8	1	8	1455.85014	2.79	14	5	10	14	6	9
1401.09152	1.68	10	4	7	11	3	8	1458.32760	3.64	5	1	5	5	2	4
1402.05550	7.02	7	1	7	8	0	8	1458.86579	8.83	10	4	7	10	5	6
1403.81328	4.82	7	2	6	8	1	7	1459.37332	1.21	13	5	9	13	6	8
1404.07273	1.45	14	2	12	14	3	11	1459.60779	11.85	1	1	0	2	2	1
1404.16855	12.78	5	1	4	6	2	5	1459.88895	13.08	8	3	6	8	4	5
1404.44493	4.24	8	0	8	8	1	7	1460.93767	16.14	4	1	4	5	0	5
1406.18821	5.06	8	3	6	9	2	7	1461.02143	3.54	9	4	6	9	5	5
1408.52951	16.80	2	2	1	3	3	0	1461.53659	1.98	11	5	7	11	6	6
1409.08604	1.87	13	3	11	13	4	10	1462.10225	10.27	8	4	5	8	5	4
1409.75918	6.91	2	2	0	3	3	1	1462.52788	3.69	7	4	4	7	5	3
1410.50143	11.06	10	2	9	10	3	8	1462.65771	8.58	6	4	3	6	5	2
1414.42229	4.93	4	1	3	5	2	4	1462.84377	5.53	5	4	1	5	5	0
1418.58240	9.11	2	1	2	3	2	1	1462.91088	6.94	8	5	4	8	6	3
1418.96250	6.24	6	0	6	7	1	7	1463.11611	8.03	7	5	3	7	6	2
1420.97884	4.78	7	1	7	7	2	6	1463.17303	3.00	6	4	2	6	5	1
1421.21597	18.54	6	1	6	7	0	7	1463.20339	6.14	7	5	2	7	6	1
1421.99372	4.30	10	1	9	10	2	8	1463.64950	7.08	9	5	4	9	6	3
1423.00307	7.16	12	3	10	12	4	9	1464.10639	5.14	7	3	5	7	4	4
1424.19468	5.80	13	2	11	13	3	10	1464.22804	10.32	7	4	3	7	5	2
1424.38630	.81	15	4	12	15	5	11	1464.45850	14.72	6	2	5	6	3	4
1426.44050	10.83	6	2	5	7	1	6	1464.61389	9.57	11	2	9	11	3	8
1426.61023	12.74	3	1	2	4	2	3	1466.14779	.82	13	6	8	13	7	7
1426.80999	4.78	9	2	8	9	3	7	1466.58456	12.93	6	3	4	6	4	3
1428.87887	12.78	7	0	7	7	1	6	1466.76994	3.70	11	6	5	11	7	4
1434.48242	3.67	14	4	11	14	5	10	1466.80517	3.29	12	6	7	12	7	6
1434.69032	3.25	11	3	9	11	4	8	1466.95753	1.10	12	6	6	12	7	5
1436.23313	17.45	5	0	5	6	1	6	1467.02914	6.93	8	1	7	8	2	6
1440.57286	13.05	6	1	6	6	2	5	1467.27126	1.27	11	6	6	11	7	5
1440.69958	7.43	5	1	5	6	0	6	1467.59683	2.60	13	6	7	13	7	6
1441.54066	14.31	8	2	7	8	3	6	1467.64568	15.46	3	0	3	4	1	4
1441.55832	5.04	2	1	1	3	2	2	1467.67372	4.35	10	6	5	10	7	4
1443.43447	1.75	13	4	10	13	5	9	1467.79748	4.09	5	3	3	5	4	2
1443.55165	1.95	12	2	10	12	3	9	1468.26679	7.20	4	3	2	4	4	1
1444.75225	13.51	9	1	8	9	2	7	1468.50961	3.96	8	6	3	8	7	2
1445.18917	10.77	10	3	8	10	4	7	1469.70394	2.64	9	6	3	9	7	2
1449.03269	5.57	12	4	9	12	5	8	1470.74865	9.93	9	4	5	9	5	4
1451.33601	2.05	15	3	12	15	4	11	1470.82570	1.60	12	5	7	12	6	6
1452.25223	3.22	5	2	4	6	1	5	1470.86842	11.08	5	3	2	5	4	1
1452.46880	6.86	4	0	4	5	1	5	1472.10832	2.90	5	2	4	5	3	3
1452.60699	4.02	1	1	1	2	2	0	1473.63930	.35	13	7	7	13	8	6
1453.61728	4.58	9	3	7	9	4	6	1473.68790	11.08	4	1	4	4	2	3
1453.78861	5.01	6	0	6	6	1	5	1473.94574	1.70	13	7	6	13	8	5

TABLE 1—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1474.53451	2.16	12	7	6	12	8	5	1502.08944	8.18	6	2	4	6	3	3
1474.62818	5.15	6	3	3	6	4	2	1502.43575	7.96	8	2	6	8	3	5
1474.64346	.84	12	7	5	12	8	4	1504.61311	20.43	7	2	5	7	3	4
1475.41670	.97	11	7	5	11	8	4	1506.02058	10.11	2	1	2	3	0	3
1475.45036	2.49	11	7	4	11	8	3	1511.48592	22.23	5	1	4	5	2	3
1476.29556	5.66	10	7	4	10	8	3	1511.85964	3.81	2	1	1	2	2	0
1476.29556	5.66	13	5	8	13	6	7	1515.29143	16.60	3	1	2	3	2	1
1477.06479	1.57	8	4	5	9	3	6	1515.67378	8.74	4	1	3	4	2	2
1477.16221	3.23	9	7	2	9	8	1	1516.66277	2.47	0	0	0	1	1	1
1477.24877	12.96	4	2	3	4	3	2	1528.31124	6.28	2	0	2	2	1	1
1478.12342	15.03	5	0	5	5	1	4	1571.15264	.79	12	4	8	13	3	11
1480.69764	14.81	7	3	4	7	4	3	1583.35634	9.88	1	1	0	1	0	1
1480.72197	4.27	13	3	10	13	4	9	1590.38145	4.65	2	1	1	2	0	2
1481.20137	6.29	4	2	3	5	1	4	1602.72990	11.52	3	1	2	3	0	3
1481.95800	5.15	10	2	8	10	3	7	1612.18108	10.93	3	0	3	2	1	2
1482.47737	5.62	2	0	2	3	1	3	1619.36022	9.78	2	1	2	1	0	1
1482.53975	5.84	3	1	3	4	0	4	1620.33588	10.26	3	2	1	3	1	2
1483.08605	1.08	13	8	5	13	9	4	1620.46942	4.93	4	2	2	4	1	3
1484.50479	8.69	11	4	7	11	5	6	1621.12388	3.48	4	1	3	4	0	4
1484.72978	1.81	12	8	5	12	9	4	1626.05912	12.78	5	2	3	5	1	4
1486.20347	4.09	3	1	3	3	2	2	1635.02654	3.42	3	1	3	2	0	2
1486.27429	1.96	11	8	3	11	9	2	1639.08384	4.18	2	2	1	2	1	2
1486.74360	19.24	7	1	6	7	2	5	1635.81429	4.17	4	0	4	3	1	3
1487.71868	1.72	10	8	3	10	9	2	1638.41534	4.06	6	2	4	6	1	5
1488.18626	5.75	8	3	5	8	4	4	1639.08384	4.18	2	2	1	2	1	2
1488.92307	2.26	15	5	10	15	6	9	1644.68809	6.84	5	1	4	5	0	5
1490.02296	5.42	4	2	2	4	3	1	1649.80753	14.84	4	1	4	3	0	3
1491.63549	2.43	12	4	8	12	5	7	1657.38967	17.13	5	0	5	4	1	1
1491.85951	.75	13	9	4	13	10	3	1657.43834	7.16	5	1	4	4	2	3
1492.91649	3.16	12	3	9	12	4	8	1657.75822	8.21	7	2	5	7	1	6
1494.53348	3.02	15	4	11	15	5	10	1660.24434	8.86	7	3	4	7	2	5
1494.61027	.82	12	9	4	12	10	3	1660.46763	5.68	4	2	3	4	1	6
1494.87164	17.26	9	2	7	9	3	6	1662.60306	2.86	6	3	3	6	2	4
1495.03786	14.95	9	3	6	9	4	5	1664.06360	2.83	8	3	5	8	2	6
1495.61165	8.00	2	1	2	2	2	1	1665.02896	7.28	5	1	5	4	0	4
1496.31088	2.34	13	4	9	13	5	8	1668.76230	7.27	5	3	2	5	2	3
1496.42783	14.59	5	2	3	5	3	2	1675.40613	4.87	9	3	6	9	2	7
1496.56629	1.39	14	4	10	14	5	9	1675.63948	6.32	2	2	1	1	1	0
1497.13872	.77	11	9	2	11	10	1	1677.22325	7.88	6	0	6	5	1	5
1498.37974	11.42	1	0	1	2	1	2	1681.09234	18.41	6	1	6	5	0	5
1498.51658	11.19	11	3	8	11	4	7	1681.30343	3.43	3	3	0	3	2	1
1498.99483	4.42	10	3	7	10	4	6	1688.92966	3.38	6	1	5	5	2	4
1499.44493	.53	10	9	2	10	10	1	1689.84970	5.03	4	3	2	4	2	3
1499.82811	6.65	4	0	4	4	1	3	1692.16188	1.15	9	4	5	8	5	4
1501.89175	8.69	6	1	5	6	2	4	1693.41719	5.08	6	2	5	6	1	6

TABLE 1—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1694.03061	2.80	3	2	2	2	1	1	1769.40583	2.58	10	4	7	10	3	8
1695.34020	1.66	5	3	3	5	2	4	1776.07231	.71	10	5	5	10	4	6
1695.77607	2.45	7	2	5	6	3	4	1778.08823	1.25	10	2	9	10	1	10
1695.85538	5.13	7	0	7	6	1	6	1778.53088	6.60	4	3	2	3	2	1
1697.73823	7.98	7	1	7	6	0	6	1780.93987	5.27	12	0	12	11	1	11
1698.69337	3.59	7	1	6	7	0	7	1780.99096	13.74	12	1	12	11	0	11
1701.08493	.96	10	4	7	9	5	4	1785.67773	.42	11	3	9	11	2	10
1703.36927	3.11	11	4	7	11	3	8	1785.89564	1.91	9	5	4	9	4	5
1703.68002	5.40	6	3	4	6	2	5	1795.14781	9.88	10	2	9	9	1	8
1707.12517	4.43	9	4	5	9	3	6	1795.72307	.39	13	5	8	12	6	7
1709.65141	8.65	4	2	3	3	1	2	1796.49769	2.03	7	5	2	7	4	3
1711.46216	3.55	9	2	7	9	1	8	1796.59179	2.19	5	3	3	4	2	2
1713.07827	1.17	7	2	6	7	1	7	1797.02709	11.82	13	0	13	12	1	12
1713.70902	7.91	8	0	8	7	1	7	1797.05340	4.52	13	1	13	12	0	12
1714.60997	18.57	8	1	8	7	0	7	1797.12803	1.14	12	4	9	12	3	10
1715.68788	4.60	3	2	1	2	1	2	1798.64949	1.15	5	5	0	5	4	1
1718.05015	9.91	7	1	6	6	2	5	1798.95738	1.71	6	5	2	6	4	3
1719.53149	2.47	11	3	8	11	2	9	1799.33717	2.02	8	5	4	8	4	5
1723.04623	3.30	5	2	4	4	1	3	1802.78610	1.67	10	2	8	9	3	7
1725.51901	4.16	7	4	3	7	3	4	1805.32519	1.53	5	2	3	4	1	4
1729.10680	2.00	9	3	6	8	4	5	1806.39107	.42	11	5	7	11	4	8
1729.14717	1.31	13	4	9	13	3	10	1809.84127	2.41	11	3	8	10	4	7
1729.43438	2.26	9	5	4	8	6	3	1810.39029	8.69	11	1	10	10	2	9
1731.03691	17.76	9	0	9	8	1	8	1810.99739	5.42	6	3	4	5	2	3
1731.46767	7.43	9	1	9	8	0	8	1812.89180	9.68	14	0	14	13	1	13
1734.06656	2.19	8	2	7	8	1	8	1813.23306	3.20	11	2	10	10	1	9
1735.30769	9.19	6	2	5	5	1	4	1814.71456	5.02	5	3	2	4	2	3
1738.49215	3.02	5	4	1	5	3	2	1816.63881	.28	12	5	8	12	4	9
1743.80284	3.36	6	4	3	6	3	4	1822.42384	1.83	7	3	5	6	2	4
1744.97001	1.18	13	5	8	13	4	9	1825.81989	.51	13	6	7	13	5	8
1747.90395	3.80	7	2	6	6	1	5	1828.51141	8.14	15	0	15	14	1	14
1747.97605	6.82	10	0	10	9	1	9	1830.22139	2.25	12	1	11	11	2	10
1748.18395	16.60	10	1	10	9	0	0	1831.72581	7.36	12	2	11	11	1	10
1749.30789	1.46	15	5	10	15	4	11	1831.99384	4.91	8	3	6	7	2	5
1751.54270	2.79	8	4	5	8	3	6	1832.92702	4.30	11	2	9	10	3	8
1756.45547	1.00	4	2	2	3	1	3	1839.14683	6.03	4	4	1	3	3	0
1758.33298	7.17	3	3	0	2	2	1	1839.32488	3.63	4	4	0	3	3	1
1762.00313	9.69	8	2	7	7	1	6	1841.12723	1.68	9	3	7	8	2	6
1764.30756	1.65	11	5	6	11	4	7	1841.43895	.60	13	4	9	12	5	8
1764.59755	15.77	11	0	11	10	1	10	1843.94731	6.58	16	1	16	15	0	15
1764.69949	6.20	11	1	11	10	0	10	1845.26948	.78	11	6	5	11	5	6
1765.30743	2.05	10	3	8	10	2	9	1849.57896	6.03	13	1	12	12	2	11
1767.98449	10.03	9	1	8	8	2	7	1849.64079	1.18	6	3	3	5	2	4
1769.34958	4.80	9	2	7	8	3	6	1850.37922	2.14	13	2	12	12	1	11

TABLE 1—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1851.33772	4.61	10	3	8	9	2	7
1855.60962	.46	12	6	7	12	5	8
1859.20097	5.70	17	0	17	16	1	6
1862.95583	1.82	5	4	2	4	3	1
1863.69106	1.44	11	3	9	10	2	8
1864.17118	5.10	5	4	1	4	3	2
1868.63790	1.70	14	1	13	13	2	12
1869.06813	4.67	14	2	13	13	1	12
1874.31259	3.28	18	1	18	17	0	17
1883.88200	.95	13	3	10	12	4	9
1884.58185	3.00	13	2	11	12	3	10
1885.02070	4.24	6	4	3	5	3	2
1887.50608	3.58	15	1	14	14	2	13
1891.55106	1.99	7	3	4	6	2	5
1895.45757	.98	13	3	11	12	2	10
1903.97972	1.29	7	4	4	6	3	3
1907.13168	.76	14	2	12	13	3	11
1916.68198	3.20	7	4	3	6	3	4
1918.85999	2.86	8	4	5	7	3	4
1920.88502	1.35	5	5	1	4	4	0
1920.91325	4.03	5	5	0	4	4	1
1924.88857	.36	15	4	11	14	5	10
1937.46076	1.95	10	4	7	9	3	6
1945.47624	3.20	6	5	2	5	4	1
1948.51257	1.32	12	4	9	11	3	8
1949.87026	.55	15	3	12	14	4	11
1957.33960	.42	13	4	10	12	3	9
1967.02102	.99	14	4	11	13	3	10
1970.25529	2.64	7	5	2	6	4	3
1981.60224	1.44	9	4	5	8	3	6
2000.90337	1.99	6	6	1	5	5	0
2071.68267	.49	11	4	7	10	3	8

To our surprise, the 1000°C spectrum in the 1000 to 2200 cm^{-1} showed many previously unobserved transitions. We have been able to identify the new $5\nu_2 - 4\nu_2$ band and considerably extend the rotational assignments in other hot bands.

II. EXPERIMENTAL DETAILS

The hot water spectra were recorded on April 9, 1993 with the Fourier transform spectrometer associated with the McMath–Pierce Telescope of the National Solar Observatory on Kitt Peak. The spectrometer was operated

with a KCl beamsplitter, Si:As detectors, and an InAs filter. The 550–2800 cm^{-1} region was covered at a resolution of 0.005 cm^{-1} .

The center of a 1 m long by 5 cm diameter alumina tube was heated to about 1000°C. The spectrum was recorded as the temperature changed from 904 to 1008°C. The tube was evacuated and the ends were sealed with cooled KBr windows. A steady flow of water vapor passed through the cell at a pressure of 0.9 Torr. The thermal emission (29) from the hot water vapor was sent into the entrance aperture of the spectrometer. Twelve scans were co-added in 61 min of integration.

The H_2O emission lines from 920 cm^{-1} to 2000 cm^{-1} were measured with the data reduction program DECOMP. Each of 4381 lines was fitted with a Voigt lineshape function. A typical linewidth of 0.008 cm^{-1} was measured and the maximum signal-to-noise ratio was about 300. The lines were calibrated by multiplication by the factor 0.999999397 obtained using the measurements of Toth (9). Strong unblended lines should have an absolute accuracy of about 0.0001 cm^{-1} .

III. ANALYSIS

We found that the sequence bands with $\Delta v_2 = 1$ were much stronger than other hot bands such as $\nu_3 + \nu_2 - \nu_3$. For example, the $3\nu_2 - 2\nu_2$ band is about 10 times stronger than the $\nu_3 + \nu_2 - \nu_3$ band although the upper levels have comparable energies and populations. This is due to the well known increase in transition dipole moment for sequence bands as the vibrational quantum number increases. For example, for a harmonic oscillator the matrix element $(\langle v + 1 | x | v \rangle)^2 = (\hbar/2m\omega)(v + 1)$ increases linearly with v . Since this matrix element is directly proportional to the intensity, it tends to offset the decreasing population (Boltzmann factor) as v increases.

The bulk of the strong lines observed belong to the ν_2 and $2\nu_2 - \nu_2$ bands reported in (7–9). Our 1000°C spectrum of the ν_2 band has some higher J, K_a transitions than reported for the room temperature spectra (7, 8) and they were assigned using energy levels determined from the flame spectra (2, 3). A few lines of the ν_2 band involved higher J, K_a levels than listed in the references (2, 3). In this case the rotational energy levels of the ground and (010) vibrational states obtained in our previous work were used (27), thus confirming the correctness of these levels. These assignments (which we call trivial) were simple to make and we will not discuss them further.

For the $3\nu_2 - 2\nu_2$ and $4\nu_2 - 3\nu_2$ bands, only a small proportion of the lines could be assigned using the published energy levels (4–9). For the $5\nu_2 - 4\nu_2$ bands there were no known energy levels, since no spectra involving the (050) state had been obtained experimentally. The nontrivial assignment of these new lines with higher J, K_a than given in the literature requires highly accurate calculations.

TABLE 2

List of H₂¹⁶O Transitions Assigned to 030-020 Hot Band (Wavenumbers in cm⁻¹, Intensities (Int) in Arbitrary Relative Units)

Wavenumber	Int	<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Wavenumber	Int	<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J</i>	<i>K_a</i>	<i>K_c</i>
1127.66069	.79	11	5	6	12	6	7	1253.40180	.49	13	2	11	14	3	12
1136.32025	.69	10	4	7	11	5	6	1256.30221	4.48	6	6	1	7	7	0
1139.07762	.40	9	3	7	10	4	6	1264.54190	1.38	13	1	12	14	2	13
1140.41900	.42	11	4	7	12	5	8	1265.57472	.95	11	2	9	12	3	10
1148.20814	1.18	10	5	6	11	6	5	1266.99332	4.73	5	4	1	6	5	2
1165.16396	.55	9	4	6	10	5	5	1270.90976	.74	12	0	12	13	3	13
1169.14485	.80	15	0	15	15	1	14	1271.04794	6.47	5	3	2	6	4	3
1170.36578	.93	10	7	4	11	8	3	1271.27318	.87	15	1	14	15	2	13
1173.49034	1.66	9	5	4	10	6	5	1271.51101	2.04	11	0	11	11	1	10
1175.35397	1.69	9	4	5	10	5	6	1271.68297	4.35	6	5	0	6	6	1
1178.31807	1.85	8	3	6	9	4	5	1272.83659	1.70	9	2	7	10	3	8
1182.58525	1.14	9	6	4	10	7	3	1275.93712	.70	8	2	6	9	3	7
1182.69493	1.60	9	6	3	10	7	4	1280.62366	2.44	7	2	5	8	3	6
1184.92686	1.00	10	8	3	11	9	2	1287.87605	1.27	14	2	13	14	3	12
1191.79687	2.31	8	4	5	9	5	4	1289.46429	2.90	11	0	11	12	1	12
1194.54418	1.17	14	1	14	14	2	13	1289.70013	1.03	11	1	11	12	0	12
1194.68486	1.90	9	7	2	10	8	3	1291.67435	5.70	4	4	1	5	5	0
1195.63331	1.34	8	5	4	9	6	3	1291.69111	2.39	4	4	0	5	5	1
1197.54153	.76	8	5	3	9	6	4	1292.94369	1.77	11	1	10	12	2	11
1202.63392	.63	11	3	8	12	4	9	1293.65466	5.35	4	3	2	5	4	1
1206.93607	2.13	8	6	3	9	7	2	1294.81374	2.58	10	1	10	10	2	9
1206.96070	.68	8	6	2	9	7	3	1297.29407	1.27	10	0	10	10	1	9
1208.62091	1.64	9	3	6	10	4	7	1298.66010	3.78	4	2	3	5	3	2
1209.34374	1.44	9	8	1	10	9	2	1299.06492	3.40	5	2	3	6	3	4
1214.96242	.90	15	0	15	16	1	16	1306.20097	.72	10	1	9	11	2	10
1217.21361	1.02	7	4	4	8	5	3	1307.89001	1.10	10	0	10	11	1	11
1218.67349	3.09	7	4	3	8	5	4	1308.30440	3.49	10	1	10	11	0	11
1219.25970	2.45	8	7	2	9	8	1	1310.64758	1.67	13	1	12	13	2	11
1221.67431	.99	7	5	3	8	6	2	1314.42293	2.09	10	2	9	11	1	10
1222.03803	3.28	7	5	2	8	6	3	1318.32509	2.47	9	1	8	10	2	9
1230.40216	.90	9	9	0	10	10	1	1318.69054	5.87	3	3	0	4	4	1
1231.52288	3.52	7	6	2	8	7	1	1318.97690	.95	9	1	9	9	2	8
1231.63348	2.83	7	3	4	8	4	5	1323.43964	3.13	9	0	9	9	1	8
1233.66604	1.30	14	1	14	15	0	15	1323.92961	1.88	12	2	11	12	3	10
1234.05727	1.96	8	8	1	9	9	0	1324.82341	.58	3	1	3	4	2	2
1235.29007	.42	15	1	14	16	2	15	1326.12301	4.04	9	0	9	10	1	10
1241.29962	3.60	6	3	4	7	4	3	1333.40542	4.69	3	2	1	4	3	2
1242.12741	4.22	6	4	3	7	5	2	1337.96451	3.26	7	1	6	8	2	7
1244.06294	3.18	7	7	0	8	8	1	1342.39332	3.30	8	1	8	8	2	7
1246.65362	3.81	6	5	2	7	6	1	1345.42299	4.60	8	1	8	9	0	9
1250.97080	.74	14	2	13	15	1	14	1345.90189	1.04	6	1	5	7	2	6
1252.27768	1.68	13	0	13	14	1	14	1350.16440	1.13	8	0	8	8	1	7
1252.35906	.73	13	1	13	14	0	14	1351.11921	2.46	8	2	7	9	1	8

TABLE 2—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c	Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1353.86777	3.15	5	1	4	6	2	5	1417.15948	1.73	8	5	4	8	6	3
1354.66043	4.64	2	2	1	3	3	0	1417.57602	2.54	5	3	2	5	4	1
1354.78074	2.43	11	1	10	11	2	9	1417.86506	1.25	7	5	2	7	6	1
1355.70434	1.58	2	2	0	3	3	1	1420.06577	3.52	4	1	4	4	2	3
1359.50573	2.90	10	2	9	10	3	8	1420.22464	1.14	6	3	3	6	4	2
1361.59216	4.61	7	0	7	8	1	8	1423.14378	4.67	4	1	4	5	0	5
1363.17036	1.00	4	1	3	5	2	4	1423.20859	4.64	3	0	3	4	1	4
1364.06965	1.52	7	1	7	8	0	8	1423.52524	3.19	4	2	3	4	3	2
1364.70073	1.08	7	1	7	7	2	6	1423.95712	1.55	8	1	7	8	2	6
1366.27416	2.31	2	1	2	3	2	1	1424.97454	3.60	7	3	4	7	4	3
1372.57365	.79	7	2	6	8	1	7	1425.06917	3.08	11	2	9	11	3	8
1374.85287	3.17	3	1	2	4	2	3	1425.10512	.61	5	2	4	6	1	5
1375.44350	1.17	9	2	8	9	3	7	1425.35117	.27	7	3	5	8	2	6
1377.50892	3.45	7	0	7	7	1	6	1426.10784	.87	10	6	5	10	7	4
1378.36313	1.12	10	1	9	10	2	8	1426.91861	.94	9	6	3	9	7	2
1378.46891	1.68	6	0	6	7	1	7	1427.55220	.83	8	6	3	8	7	2
1382.99136	4.91	6	1	6	7	0	7	1427.75982	1.82	11	4	7	11	5	6
1385.42976	3.53	6	1	6	6	2	5	1428.29355	.70	7	6	1	7	7	0
1389.07365	.88	13	2	11	13	3	10	1430.63302	2.14	3	2	1	3	3	0
1389.51923	1.08	2	1	1	3	2	2	1430.82943	4.52	5	0	5	5	1	4
1389.68321	3.76	8	2	7	8	3	6	1434.98215	1.15	4	2	2	4	3	1
1394.54779	3.08	10	3	8	10	4	7	1437.21125	1.16	2	0	2	3	1	3
1397.12811	2.24	6	2	5	7	1	6	1438.95723	3.50	9	3	6	9	4	5
1400.26400	.97	1	1	1	2	2	0	1440.02224	.58	9	7	2	9	8	1
1401.79710	1.39	7	2	6	7	3	5	1441.11098	.38	8	7	2	8	8	1
1402.01075	3.89	9	1	8	9	2	7	1441.30005	4.50	5	2	3	5	3	2
1402.51602	1.69	5	1	5	6	0	6	1442.20935	5.69	7	1	6	7	2	5
1402.95359	1.00	9	3	7	9	4	6	1442.87820	1.93	2	1	2	2	2	1
1404.90574	1.24	6	0	6	6	1	5	1445.46436	1.20	3	1	3	4	0	4
1407.39972	3.21	1	1	0	2	2	1	1447.77729	2.41	11	3	8	11	4	7
1408.37861	3.35	8	3	6	8	4	5	1447.86172	1.36	6	2	4	6	3	3
1409.26253	1.62	4	0	4	5	1	5	1448.76806	4.41	9	2	7	9	3	6
1409.42394	2.03	10	4	7	10	5	6	1452.37314	5.26	7	2	5	7	3	4
1412.00806	1.23	7	3	5	7	4	4	1452.66247	2.93	1	0	1	2	1	2
1412.42403	2.46	8	4	5	8	5	4	1453.00051	1.67	8	2	6	8	3	5
1413.03418	.73	7	4	4	7	5	3	1453.16771	1.56	4	0	4	4	1	3
1413.42572	2.11	6	4	3	6	5	2	1456.06461	.31	9	8	1	9	9	0
1413.73571	.71	6	4	2	6	5	1	1464.16794	4.24	3	1	2	3	2	1
1413.81946	1.17	5	4	1	5	5	0	1465.74719	1.93	4	1	3	4	2	2
1414.07127	2.42	7	4	3	7	5	2	1469.78102	2.48	2	1	2	3	0	3
1414.17885	3.25	6	3	4	6	4	3	1470.28622	4.82	3	0	3	3	1	2
1414.99618	1.34	10	5	6	10	6	5	1481.85583	1.76	2	0	2	2	1	1
1415.32485	.95	5	3	3	5	4	2	1488.66296	3.71	1	0	1	1	1	0
1415.54408	.83	9	5	4	9	6	3	1548.10374	2.44	1	1	0	1	0	1

TABLE 2—Continued

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1555.25559	.59	2	1	1	2	0	2
1566.99559	2.72	3	0	3	2	1	2
1567.67474	3.17	3	1	2	3	0	3
1583.58221	2.57	2	1	2	1	0	1
1596.64498	2.34	3	2	1	3	1	2
1598.57738	3.56	5	2	3	5	1	4
1612.88773	4.28	4	1	4	3	0	3
1614.57982	4.99	5	0	5	4	1	4
1617.38162	.96	2	2	1	2	1	2
1642.61408	5.39	6	1	6	5	0	5
1654.98629	5.62	7	0	7	6	1	6
1658.81605	2.03	7	1	7	6	0	6
1673.48365	1.98	8	0	8	7	1	7
1673.52702	2.41	7	1	6	6	2	5
1691.33709	5.42	9	0	9	8	1	8
1692.41880	2.00	9	1	9	8	0	8
1709.33792	4.87	10	1	10	9	0	0
1711.00956	2.43	6	2	5	5	1	4
1725.86293	4.16	11	0	11	10	1	10
1729.81972	2.29	9	1	8	8	2	7
1733.71927	.21	4	2	2	3	1	3
1734.93345	2.16	8	2	7	7	1	6
1742.91705	3.28	12	1	12	11	0	11
1759.43036	2.99	13	0	13	12	1	12
1759.53557	.95	13	1	13	12	0	12
1769.89119	2.93	4	3	2	3	2	1
1776.05534	2.43	14	1	14	13	0	13
1792.46447	1.65	15	0	15	14	1	14
1802.77193	1.10	6	3	4	5	2	3
1804.49839	1.10	5	3	2	4	2	3
1820.16236	1.32	13	1	12	12	2	11
1841.54798	1.17	4	4	1	3	3	0
1842.35037	1.03	14	2	13	13	1	12
1849.95264	.62	13	2	11	14	3	12
1861.66620	.82	15	1	14	16	2	13

For example, the water in the sunspot spectrum has an effective temperature of about 2800°C and has an average line density of nearly 50 lines/cm⁻¹. The present spectrum has a line density of 5–10 lines/cm⁻¹, which makes the new assignments easier than for the sunspot spectrum. In our previous paper (27) we have used an effective Hamiltonian in a Padé–Borel form (18) for the calculation of the high J , K_a energy levels of water in the ground

and (010) excited vibrational state. Variational calculations, however, have been demonstrated to have better extrapolation properties than an effective Hamiltonian approach (20). Variational calculations also calculate energy levels involving all the vibrational states at one time, automatically solving the problem of the accidental resonances between various vibrational states, which have to be included explicitly for every resonance in an effective Hamiltonian matrix approach. These two properties make variational calculations invaluable for assigning highly excited rovibrational levels of water.

To assign the hotter transitions observed here, we used a variational calculation based on the exact kinetic energy (EKE) approach. These calculations use a high accuracy *ab initio* Born–Oppenheimer potential energy surface due to Partridge and Schwenke (30). This potential was then modified by the addition of an *ab initio* mass-dependent surface representing the adiabatic correction to the Born–Oppenheimer approximation (31). Nonadiabatic effects have also been shown to be important for rotationally excited water (22); these were introduced phenomenologically by using a hydrogenic mass intermediate between atomic H and the proton (see (31)). A full treatment of the effects of Born–Oppenheimer breakdown in water will be the subject of future work (32).

Nuclear motion calculations were performed using the DVR3D program suite (33) using basis sets developed for previous studies (22). To bring the *ab initio* estimates of the transition frequencies into line with the observations, each rovibrational energy level was adjusted by the difference between the observed and calculated band origin for the vibrational level in question.

In a table which is available from the author or editor on request, we present the observed ν_2 , $2\nu_2 - \nu_2$, $3\nu_2 - 2\nu_2$, $4\nu_2 - 3\nu_2$, and $5\nu_2 - 4\nu_2$ hot band lines. More than 1700 lines of the total 4381 lines were assigned. Some of them are identical to the room temperature water spectrum of ν_2 and $2\nu_2 - \nu_2$, presented in (8), (9).

Lines with lower J belonging to ν_2 , which are strong in room temperature spectra, suffered from self absorption caused by cooler water at the ends of the cell, atmospheric water, and trace amounts of water in the spectrometer. Because of the Doppler effect, the high temperature emission lines are broader than the cooler absorption lines. The cooler water thus removes the line center from the emission lines, resulting in doublet line artifacts (see Ref. (1) for an example). As a rule, the line centers of these doublets were found to be shifted to the right and to the left by approximately 0.005 cm⁻¹ from the line center of the room temperature transition.

Transitions assigned to $2\nu_2 - \nu_2$, $3\nu_2 - 2\nu_2$, $4\nu_2 - 3\nu_2$, and $5\nu_2 - 4\nu_2$ bands are given in Tables 1, 2, 3, and 4, respectively. More than half of the measured lines remain unassigned and they belong to the other hot bands and to higher J 's and K_a 's of the ν_2 manifold of hot bands. The

TABLE 3
List of H₂¹⁶O Transitions Assigned to 040-030 Hot Band (Wavenumbers in cm⁻¹,
Intensities (Int) in Arbitrary Relative Units)

Wavenumber	Int	J'	K' _a	K' _c	J	K _a	K _c	Wavenumber	Int	J'	K' _a	K' _c	J	K _a	K _c
1126.45276	.32	8	3	6	9	4	5	1321.26576	.91	6	1	6	6	2	5
1141.10040	.45	8	4	5	9	5	4	1321.97624	.48	7	1	7	8	0	8
1167.64853	.58	7	4	3	8	5	4	1330.86730	.30	6	0	6	7	1	7
1170.75644	.57	7	3	4	8	4	5	1332.07540	.98	8	2	7	8	3	6
1176.86438	.52	7	5	2	8	6	3	1340.88493	1.25	6	1	6	7	0	7
1185.51367	.74	6	3	4	7	4	3	1344.91368	1.15	5	0	5	6	1	6
1191.40876	.84	6	4	3	7	5	2	1345.76772	.73	1	1	0	2	2	1
1191.64662	.23	6	4	2	7	5	3	1352.42177	.67	8	3	6	8	4	5
1192.18003	.65	7	6	1	8	7	2	1356.00212	.98	9	1	8	9	2	7
1201.60277	.56	11	0	11	11	1	10	1357.16937	.75	4	1	4	4	2	3
1201.84950	.71	6	5	2	7	6	1	1357.45781	.65	6	3	4	6	4	3
1203.35011	.33	6	5	1	7	6	2	1357.93971	.73	4	0	4	5	1	5
1206.44720	.29	9	2	7	10	3	8	1360.08656	.54	5	3	2	5	4	1
1211.77099	.36	5	3	3	6	4	2	1362.65727	.50	4	2	3	4	3	2
1213.65445	.99	5	3	2	6	4	3	1362.77039	.33	7	4	3	7	5	2
1216.30800	.86	5	4	2	6	5	1	1364.50599	.69	7	3	4	7	4	3
1216.36076	.91	5	4	1	6	5	2	1368.73517	.40	3	2	1	3	3	0
1217.07076	.77	6	6	0	7	7	1	1370.49875	1.17	3	0	3	4	1	4
1225.08394	1.09	10	1	10	10	2	9	1371.80461	.36	6	2	5	7	1	6
1226.98986	.92	5	5	0	6	6	1	1372.89352	.20	7	5	2	7	6	1
1234.65896	.75	5	2	3	6	3	4	1375.43387	.54	9	3	6	9	4	5
1237.14739	1.15	4	3	2	5	4	1	1376.47529	1.05	5	0	5	5	1	4
1237.62162	.33	4	3	1	5	4	2	1380.76026	.31	2	1	2	2	2	1
1238.73574	.90	4	2	3	5	3	2	1389.22852	.19	7	6	1	7	7	0
1241.20767	1.25	4	4	1	5	5	0	1390.54939	1.08	7	2	5	7	3	4
1249.38211	.55	11	0	11	12	1	12	1390.65323	1.38	7	1	6	7	2	5
1259.82688	.56	9	0	9	9	1	8	1393.37265	.98	9	2	7	9	3	6
1262.19107	1.13	3	3	0	4	4	1	1398.72881	.67	1	0	1	2	1	2
1267.98966	.80	10	1	10	11	0	11	1403.62214	.95	3	1	2	3	2	1
1269.33309	.47	9	1	8	10	2	9	1406.03554	1.48	5	1	4	5	2	3
1271.54659	1.04	3	2	1	4	3	2	1415.71186	1.19	3	0	3	3	1	2
1276.00036	.88	8	1	8	8	2	7	1415.87900	1.67	4	3	2	4	4	1
1281.59410	.77	7	1	6	8	2	7	1431.14611	.57	2	1	2	3	0	3
1283.33774	.98	9	0	9	10	1	10	1434.20708	.64	1	0	1	1	1	0
1289.87755	.37	8	0	8	8	1	7	1513.60605	.48	3	0	3	2	1	2
1293.59678	1.14	5	1	4	6	2	5	1529.98006	.80	3	1	2	3	0	3
1294.41961	.39	2	2	0	3	3	1	1545.47912	.53	2	1	2	1	0	1
1299.56695	.31	7	1	7	7	2	6	1548.67574	.32	5	1	4	4	2	3
1299.84194	.34	8	0	8	9	1	9	1564.38379	1.11	5	0	5	4	1	4
1303.67963	1.12	8	1	8	9	0	9	1577.27426	1.80	3	2	1	3	1	2
1304.46806	.75	10	2	9	10	3	8	1587.16665	.40	6	0	6	5	1	5
1304.78743	.67	2	1	2	3	2	1	1601.44568	1.23	6	1	6	5	0	5
1313.50234	.77	3	1	2	4	2	3	1608.29629	1.31	7	0	7	6	1	6
1315.77048	1.02	7	0	7	8	1	8	1628.19156	.41	8	0	8	7	1	7
1320.19886	.98	7	0	7	7	1	6	1633.42481	1.38	8	1	8	7	0	7
1320.63634	.53	8	2	7	9	1	8	1647.25302	1.03	9	0	9	8	1	8

TABLE 4

List of H_2^{16}O Transitions Assigned to 050–040 Hot Band (Wavenumbers in cm^{-1} , Intensities (Int) in Arbitrary Relative Units)

Wavenumber	Int	J'	K'_a	K'_c	J	K_a	K_c
1177.44954	.26	4	3	2	5	4	1
1190.69089	.27	4	4	1	5	5	0
1201.40493	.26	3	2	1	4	3	2
1202.50215	.26	3	3	0	4	4	1
1224.35223	.25	2	2	1	3	3	0
1229.50799	.27	2	1	2	3	2	1
1237.81949	.25	3	1	2	4	2	3
1280.81905	.36	5	0	5	6	1	6
1295.04801	.17	6	1	6	7	0	7
1302.73650	.21	3	0	3	4	1	4
1308.48187	.26	5	0	5	5	1	4
1328.92729	.25	3	1	2	3	2	1
1335.60582	.32	5	1	4	5	2	3
1346.40479	.25	3	0	3	3	1	2
1347.58472	.21	0	0	0	1	1	1
1364.94591	.11	1	0	1	1	1	0
1445.24151	.15	3	0	3	2	1	2
1447.58464	.18	1	1	0	0	0	0
1499.99137	.21	5	0	5	4	1	4

assignment of these lines will be the next step in our analysis of the higher temperature spectrum (1550°C) spectrum, which is now in progress.

A very effective means of compressing the information on thousands of lines is to derive energy levels from the transitions reported in the unpublished table previously referred to. The energy levels of the (020), (030) and (040) vibrational states are presented in Tables 5–7. We do not present here the energy levels of the ground and (010) states, since all the transitions observed here are of lower J and K_a than in our previous work (27). There is one important point concerning these states which should be mentioned. One motivation for this study was to check the energy levels of the (000) and (010) states obtained in (27). Indeed we have found that the assignment of two lines in the $v_2 = 1$ state should be interchanged. In particular, the $17_{170}-16_{161}$ transition of (010) is now at 722.9167 cm^{-1} , and $17_{161}-16_{152}$ is at 722.3721 cm^{-1} . This leads to the corresponding change of energy levels in (27). A more complete discussion of the corrections to Ref. (27) will appear in another paper (34).

The comparison of the energy levels of the (020), (030), and (040) vibrational states taken from the literature with

those obtained in this work (Tables 5–7) shows that significantly higher J and K_a levels are derived in this study. The energy levels for (030) (4) and (040) (5) are confirmed in this study, whereas some levels in the (020) state (9) are derived from misassigned transitions. The levels presented in Tables 5–7 are involved as a rule in two and often three transitions (P , Q , and R branches), which confirms our assignments.

We decided not to present the energy levels of the (050) state, since at this stage only a few of them could be derived from the list of $5\nu_2 - 4\nu_2$ transitions (Table 4). From the lines in Table 4 one can see that only three levels (5_{05} , 3_{03} , and 3_{12}) are involved in more than one transition. These three levels should be considered as definitely established, since combination difference confirm the assignment. The assignment of the other lines are not so reliable and their assignment should be considered as tentative. Among these lines is the $0_{00}-1_{11}$ transition which gives a value of the (050) band origin equal to 7542.39 cm^{-1} . A more reliable source of information on the band origin is the levels confirmed by combination differences. The difference between the calculated and experimentally derived energies for these levels is constant to within 0.05 cm^{-1} . In this spirit we consider our value of the $5\nu_2$ band origin as $7542.39 \pm 0.05 \text{ cm}^{-1}$.

This is significantly different, 10 cm^{-1} , from the value predicted by the “dark state” perturbative analysis of Ulenikov and Ushakova (23). This value has been used (24) for the fitting of the water PES to the set of 70 experimental band origins (levels with $J = 0$) present in HITRAN data base (25). As has been commented on (26), the use of the value of 7552 cm^{-1} for (050) band origin might be one reason this potential (24) performs so badly for excited J calculations. Even for the moderately excited $J = 10$ this potential gives a discrepancy of about 100 cm^{-1} for (000) and (010) states (26), while the standard deviation for the fitted band origins is very good, $\sim 1 \text{ cm}^{-1}$.

Indeed, our newly determined $5\nu_2$ band origin is very much in line with values predicted by Polyansky *et al.* (22) from a variational fit to the available data on H_2O with $J \leq 14$. These workers found that they could not reproduce the high value for the $5\nu_2$ band origin obtained from the dark state analysis and predicted that the actual value was significantly lower.

After submission of our paper, we obtained two additional papers on the bending levels of water. Starikov (35) has applied a new Hamiltonian model for the energy levels of the (020), (001) and (100) states and his calculations are in accord with our measurements. Mikhailenko *et al.* (36) have analyzed the $2\nu_2$ overtone band and extended the known energy levels in the (020) state. They cover a similar range of J and K_a levels for this particular vibrational state as reported here based on the $2\nu_2 - \nu_2$ hot band and their work is also in agreement with our measurements.

TABLE 5
Energy Levels in cm⁻¹ of (020) Vibrational State of H₂¹⁶O Derived from the
Experimental Line Frequencies of Table 1

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Ref.[9]	This work	<i>J</i>	<i>K_a</i>	<i>K_c</i>	Ref.[9]	This work
9	9	1	5748.51286	5749.925	13	8	5		6602.463
9	9	0	5748.51286	5749.925	13	9	4		6873.413
10	8	3	5728.02500	5728.655	14	0	14	5204.01500	5204.023
10	8	2	5728.02500	5728.655	14	1	14	5204.01570	5204.023
10	9	2	5994.37695	5996.648	14	1	13		5522.857
10	9	1	5994.37695	5996.648	14	2	13		5523.120
					14	2	12	5786.85327	5786.856
					14	3	12	5790.43269	5790.435
11	6	6	5505.48824	5505.623	14	3	11		5993.200
11	7	5	5741.19043	5741.391	14	4	11		6019.834
11	7	4	5741.36145	5741.426	14	4	10	6134.94002	6134.919
11	8	3		5997.178	14	5	10		6229.895
11	9	2		6266.364					
					15	0	15	5483.99625	5483.998
12	5	7	5596.31840	5596.426	15	1	15	5483.99625	5483.998
12	6	7	5795.73063	5796.125	15	1	14		5827.342
12	6	6		5796.452	15	2	14		5827.487
12	7	6		6032.083	15	2	13		6113.514
12	7	5		6032.203	15	3	13		6115.680
12	8	5		6288.553	15	3	12	6345.92236	6345.928
12	8	4		6288.553	15	4	12		6362.644
12	9	4		6558.754	15	4	11		6510.239
12	9	3		6558.754	15	5	10		6641.891
13	2	12	5236.01263	5236.433	16	0	16		5781.522
13	3	11	5483.28000	5483.125	16	1	16		5781.525
13	4	10	5695.67200	5695.883	16	2	15		6149.502
13	5	9		5896.742	16	3	14		6458.013
13	5	8		5919.009					
13	6	8		6109.530	17	0	17		6096.520
13	6	7		6111.468	17	1	16		6489.057
13	7	7		6345.588					
13	7	6		6345.926	18	0	18		6428.967

Note. For $J < 14$, only levels which differ from those in Toth (9) are presented. For $J \geq 14$, all available experimental energy levels are given.

TABLE 6
 Energy Levels in cm^{-1} of (030) Vibrational State of H_2^{16}O Derived from the Experimental Line Frequencies of Table 2 (The Results of Flaud *et al.* (4) Are Given for Comparison)

J	K_a	K_c	Ref.[4]	This work	J	K_a	K_c	Ref.[4]	This work
7	0	7	5256.8462	5256.845	9	5	4		6411.877
7	1	7	5258.8677	5258.869	9	6	4		6656.398
7	1	6	5409.6949	5409.698	9	6	3		6656.499
7	2	6	5435.4065	5435.412	9	7	2		6923.341
7	2	5	5505.2044	5505.210	9	8	1		7205.992
7	3	5	5598.5798	5598.578					
7	3	4	5613.3704	5613.369	10	0	10	5777.6921	5777.686
7	4	4		5781.581	10	1	10	5778.0399	5778.041
7	4	3	5782.7027	5782.708	10	1	9	6022.5774	6022.579
7	5	3		5996.763	10	2	9	6029.2433	6029.241
7	5	2	5996.8428	5996.843	10	3	8		6237.679
7	6	2	6240.4889	6240.486	10	4	7		6436.499
7	6	1	6240.4919	6240.486	10	5	6		6653.383
7	7	1		6505.535	10	6	5		6899.912
7	7	0		6505.535					
					11	0	11	5986.3337	5986.329
8	0	8	5413.0034	5413.002	11	1	11	5986.5544	5986.534
8	1	8	5414.1282	5414.127	11	1	10	6260.4617	6260.432
8	1	7	5597.1851	5597.183	11	2	9		6459.457
8	2	7	5614.2843	5614.269	11	3	8		6592.187
8	2	6		5712.877	11	4	7		6727.939
8	3	6	5790.1125	5790.114	11	5	6		6923.790
8	3	5		5818.326					
8	4	5	5976.4553	5976.459	12	0	12		6212.532
8	5	4	6191.9705	6191.965	12	1	12	6212.6669	6212.655
8	5	3		6192.245	12	2	11		6517.812
8	6	3		6436.516					
8	7	2		6702.583					
8	8	1		6983.983	13	0	13		6456.294
					13	1	13		6456.372
					13	1	12		6787.653
9	0	9	5586.5915	5586.590	13	2	11		7043.836
9	1	9	5587.2237	5587.218					
9	1	8	5801.5502	5801.553					
9	2	8	5812.3839	5812.384	14	1	14		6717.665
9	2	7		5942.573	14	2	13		7078.312
9	3	7		6003.451					
9	3	6		6050.753	15	0	15		6996.487
9	4	5		6202.429	15	1	14		7384.788

TABLE 7
Energy Levels in cm⁻¹ of (040) Vibrational State of H₂¹⁶O Derived from the Experimental Line Frequencies of Table 4

<i>J</i>	<i>K_a</i>	<i>K_c</i>	Ref.[10]	This work
5	0	5	6466.51394	6466.515
5	1	5	6478.79942	
5	1	4	6570.06667	6570.065
5	2	4	6642.48528	
5	2	3	6664.35388	6664.353
5	3	3	6822.86883	6822.860
5	3	2	6824.41885	6824.420
5	4	2	7041.95768	7041.954
5	4	1	7041.99355	7041.983
5	5	0		7295.494
6	0	6	6589.73539	6589.744
6	1	6	6597.73020	6597.732
6	1	5	6722.49989	
6	2	5	6781.50254	6781.500
6	2	4	6821.63438	
6	3	4	6968.22280	6968.217
6	3	3	6972.60822	
6	4	3	7188.25219	7188.252
6	4	2	7188.41097	7188.410
6	5	2		7442.342
6	6	0		7722.606
7	0	7	6729.89704	6729.897
7	1	7	6734.97866	6734.980
7	1	6	6895.86351	6895.858
7	2	6	6941.63554	
7	2	5	7003.91922	7003.918
7	3	5	7135.52324	
7	3	4		7147.214
7	4	3		7359.614
7	5	2		7613.381
7	6	1		7894.764
8	0	8	6887.06034	6887.060
8	1	8	6890.27038	6890.270
8	1	7	7087.46541	
8	2	7	7122.18928	7122.189
8	2	6	7212.60000	
8	3	6	7328.88030	7328.881
8	4	5		7552.977
9	0	9	7061.37991	7061.378
9	1	9	7063.42138	
9	1	8	7297.74400	7298.576
9	2	8	7321.84080	
9	2	7		7444.126
9	3	6		7577.864

Note. The levels are given for the values of *J* where higher *K_a* levels are obtained in this work than in Ref. (10). The levels of Ref. (10) are given for comparison.

IV. CONCLUSION

We have observed hot bands of water in the ν_2 manifold in a spectrum recorded at 1000°C. A total of 4381 lines have been measured, belonging mainly to the ν_2 , $2\nu_2 - \nu_2$, $3\nu_2 - 2\nu_2$, $4\nu_2 - 3\nu_2$, and $5\nu_2 - 4\nu_2$ bands. The rotational analysis of the $\nu_2 = 2, 3$, and 4 vibrational levels has been extended to higher quantum numbers. The experimental derivation of the energy levels of $\nu_2 = 5$ has been made from the lines of the $5\nu_2 - 4\nu_2$ hot band.

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