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Spectroscopy from first principles: a breakthrough in water line assignments

Oleg L. Polyansky [1], Jonathan Tennyson *, Nikolai F. Zobov[1]

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

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Abstract

Variational calculations of the spectrum of both hot and room temperature water vapor have led to a major increase in the number and scope of observed vibration–rotation transitions that have full quantum number assignments. The calculations are performed using high accuracy ab initio potential energy surfaces. As demonstrated, it is also necessary to consider corrections due to adiabatic effects, non-adiabatic effects and the relativistic motions of the electrons. The result of this work has been to double the number and energy range of the measured energy levels for water. New energy levels for the (010), (100), (020), (001), (110), (030), (011), (040), (050) and (060) states are presented here. Analysis of these levels and the associated transitions shows unanticipated features, including rotational difference bands, and an absence of clustering. The prospects of observing quantum monodromy in the spectrum of water are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water is probably the key molecule in promoting life itself. The spectrum of water vapor is important for the transmission of solar radiation through Earth's atmosphere, the modeling of flames and exhaust gases, understanding the atmospheres of cool stars and brown dwarfs and many other applications too numerous to mention. It is, therefore, not surprising that the vibration–rotation spectrum of water vapor, which lies mostly in the infrared (IR), has been the subject of intense study for decades. Databases of water lines, such as HITRAN [1], compiled for modeling atmospheric and other process contain over 30 000 water lines, largely determined from laboratory measurements.

However, despite all these endeavors, there still remains significant problems over the interpretation of a whole variety of spectra recorded in water vapor. A number of spectra [2–8] have remained in the open literature unassigned, sometimes for a decade or more. Many other spectra were considered too hard to analyze and therefore remain unpublished.

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* Corresponding author. Tel.: +44-171-380-7809; fax: +44-171-380-7145; E-mail: j.tennyson@ucl.ac.uk.

[1] Permanent address: Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizhnii Novgorod, Russia 603024.

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Recently, there has been a major breakthrough in the analysis and assignment of IR spectra of water vapor. This breakthrough has arisen as a direct consequence of a paradigm shift in the theoretical techniques used to analyze the spectra [9]. This shift has been from theories based on perturbative expansions of effective Hamiltonians to variational calculations and the use of increasingly accurate first principles formulation of the problem.

Variational calculations for the nuclear motion of triatomics are not new. Indeed, much of the pioneering work dates back 20 years or more [10]. What is new is the accuracy with which these calculations can be performed, allowing spectra with line densities as high as 50 per cm^{-1} to be successfully analyzed [9,11].

In this paper the theoretical advances necessary to achieve these results are discussed, new compilations of measured water energy levels that have arisen from this work are presented and a number of unanticipated features found in the water spectra analyzed are also discussed. Finally, the prospects for further significant advances on this fundamental and challenging molecule are discussed.

2. Theory

2.1. Overview

It is customary to break the first principles calculation of vibration–rotation spectra into two steps comprising electronic structure and nuclear motion. This separation of the motions relies on the well-known Born–Oppenheimer approximation, which is assumed to be reliable for molecules such as water for which the nuclear motion occurs on a single, well-separated electronic state.

Within the Born–Oppenheimer approximation, it is generally possible to solve the nuclear motion problem to a considerably higher accuracy than that which the potential energy surface can be determined from electronic structure calculations. For this reason, there have been a series of studies (see [12–16] for examples) that have used spectroscopic data to determine high accuracy potential energy surfaces, using ab initio electronic structure calculations as a starting point. The better of these surfaces are more accurate, in absolute terms, than any that can at present be determined ab initio. Although spectroscopically determined surfaces have been found to extrapolate much more reliably than standard perturbation theory-based effective Hamiltonian treatments [14], uncertainty as to what such surfaces represent also leads to uncertainty in their extrapolation behavior. For this reason, completely ab initio determinations of vibration–rotation energy levels can be more helpful in analyzing unassigned spectra.

The spectra of water that this paper is interested in analyzing arise across the whole of the IR and for temperatures ranging from room temperature to 3200 K. These spectra, therefore, display a range of complexities and densities. The densest spectra addressed so far contain up to 50 well-resolved and reproducible transitions per cm^{-1}. Experience [17] has shown that, for hydrogen-containing molecules, the Born–Oppenheimer approximation is not reliable for accuracies better than 1 cm^{-1}. This level of accuracy is often described as ‘spectroscopic’ in the quantum chemistry literature, but is clearly insufficient for analyzing high resolution spectra of a molecule such as water.

2.2. Ab initio potential energy surfaces

Recent advances in quantum chemical calculations have raised the possibility of performing electronic structure calculations on small molecules to so-called spectroscopic accuracy (see [18] and other articles in this issue). However, this limit has yet to be achieved for water.

Much effort has been expended in developing size-consistent [19] and size-extensive [20] electronic structure methods. The main thrust of this work is for correct estimation of dissociation energies, but clearly the stretching frequencies in water will be sensitive to the treatment of the path to dissociation. However, it has long been recognized [21] that it is the bending frequencies in water that are the hardest to reproduce. This is probably because as water bends it also undergoes rehybridization, from sp^3 at equilibrium to sp at linearity, meaning that considerable effort is required to treat all geometries even-handedly.

Recently, Császár et al. [22] have undertaken a systematic study of the convergence of ab initio calculations when it comes to determining internal barrier heights for a number of molecules. Their study included the barrier to linearity of water. Császár et al. considered basis set effects, both for uncorrelated and correlated wavefunctions, the effect of different correlation models and the effect of correlating the core, oxygen 1s, electrons. They found that whereas most of these effects are reliably modeled with present day state-of-the-art electronic structure calculations, increasing the size of the basis set has a significant effect on the correlation energy, and that this energy is not converged with the best calculations presently available.

Predictions of water spectra have long provided a benchmark for ab initio studies, see [21] for a discussion of earlier work. Martin et al. [25] performed high level calculations of spectroscopic constants. A series of very recent high accuracy studies has been performed by Partridge and Schwenke (PS) [16], Kedziora and Shavitt [26], and Császár and Mills [27]. The results presented below all use PS's ab initio potential energy surface, which is the most extensive and accurate of these studies.

2.3. Nuclear motion calculations

It has been known for sometime [13] that to obtain reliable vibration–rotation energy levels for water it is necessary to use a so-called exact kinetic energy (EKE) nuclear motion Hamiltonian. There are a number of EKE operator Hamiltonians available for triatomic systems. For water, the most natural Hamiltonians to use are body-fixed ones based on either bond length–bond angle or Radau co-ordinates.

Bond length–bond angle co-ordinates clearly coincide closely with ones physical insight into the motions of water, but the Radau co-ordinate kinetic energy operator is considerably simpler. Three-particle Radau co-ordinates consist of two distances, r_1 and r_2, and their internal angle. Since for water these are very close to bond length–bond angle co-ordinates, the authors have worked exclusively with Radau co-ordinates.

In addition, the Hamiltonian uses the so-called bisector embedding to body-fix the axis system for rotational motion [28]. For water at equilibrium, this embedding orients the axes along the principle axes of rotation and it should, therefore, provide a good framework in which to work. However, the bisector embedding raises technical problems with linear geometries, where the Hamiltonian becomes singular [28]. Fortunately, these can be solved by judicious use of a discrete variable representation (DVR) based procedure [29].

Calculations reported here were, therefore, performed using an updated [30] version of the DVR3D program suite [31], which computes transition frequencies and intensities for given potential energy and dipole surfaces. DVR3D represents all three co-ordinates using DVR grids. For water, there is a symmetry between the two stretching co-ordinates. There is a subtle but important difference between how this symmetry is treated in DVR3D and by other workers using DVR-based techniques.

Light and co-workers [32,33] have symmetrized their DVR wavefunctions by working in symmetrized co-ordinate systems and choosing basis sets with the appropriate symmetry properties prior to transforming to the DVR. In the case of water, this means defining new co-ordinates:

$$s = \frac{1}{\sqrt{2}}(r_1 + r_2),$$
$$t = \frac{1}{\sqrt{2}}(r_1 - r_2). \tag{1}$$

Tennyson and co-workers [29,34] have instead employed basis set representations in the original co-ordinates, which are transformed to the DVR and then symmetrized:

$$|\alpha, \beta, q\rangle = \frac{1}{\sqrt{2(1+\delta_{\alpha,\beta})}}(|\alpha, \beta\rangle + (-1)^q|\beta, \alpha\rangle)$$
$$\alpha \geq \beta + q, \quad q = 0, 1, \tag{2}$$

where α and β are the radial grids, and q is the symmetry quantum number. Of course, in this approach grids used for the r_1 and r_2 co-ordinates must be the same.

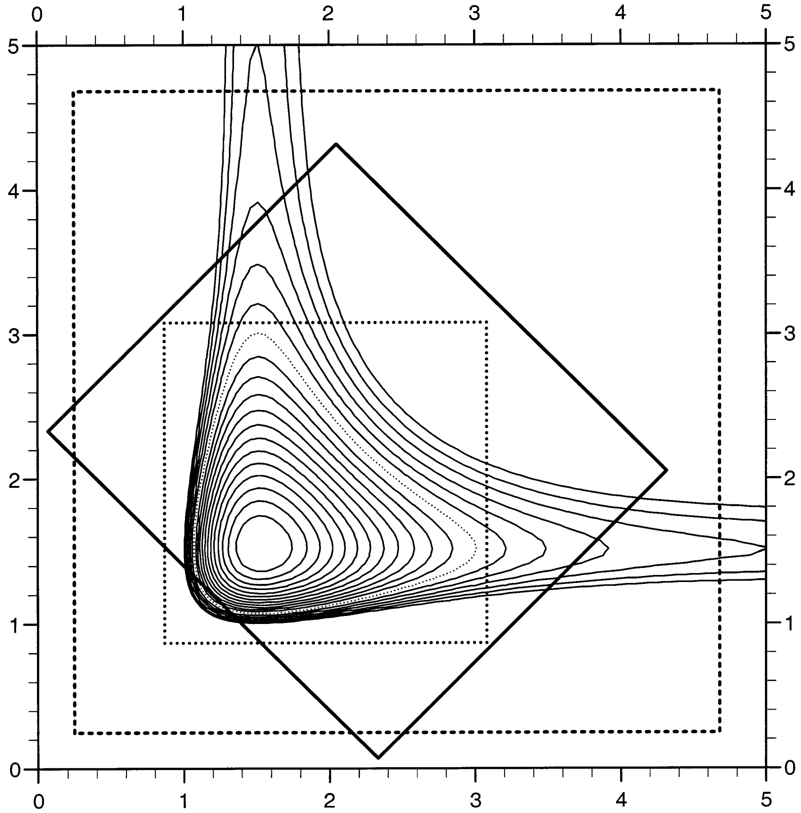

Fig. 1. Comparison of DVR grid ranges due to Fulton [35]. The plot is for Radau co-ordinates with r_1 vs. r_2 in a_0 with θ fixed at 100°. The contours represent the water potential due to Jensen [12] and are spaced by 2500 cm^{-1}. The solid box shows the range of the DVR employed by Choi and Light [33]. The dashed boxes show the range of points used in the authors' small and large calculations.

Fig. 1 illustrates the differences between these two approaches. The slanted box encloses the range of the DVR employed by Choi and Light [33] who based their DVR on (s, t, θ) co-ordinates. The other two boxes represent the range of this paper's small DVR, used for the ZVPT line list discussed below, and larger DVR, used for the much more extensive VT2 line list [30]. For highly excited states, DVR grids based on the co-ordinates of Eq. (1) have coupled integration ranges as points with $t > s$ lie outside the physical domain of the problem. In practice, this consideration has limited the range of DVR grids employed. It can be seen from Fig. 1 that increasing the size of the grid, while keeping to the physical domain of the problem, puts most points in the high energy region, where r_1 and r_2 are both large. Such grids are inappropriate for high-lying stretching modes [35]. Within the current method, it is easier to put grid points in the important region where only one stretching co-ordinate becomes large.

2.4. Beyond the Born–Oppenheimer approximation

To obtain results accurate enough to analyze the water spectra, it is necessary to move beyond the Born–Oppenheimer, non-relativistic treatment of the electronic structure problem.

Work on the first principles IR spectrum of H_3^+ [36,37] has suggested that the adiabatic or diagonal Born–Oppenheimer correction (BODC) might have a significant influence on the calculated transition frequencies. This term can be evaluated fairly easily using an electronic structure program that computes second derivatives with respect to nuclear co-ordinates [38]. However, tests have shown that the BODC has little influence on the vibrational energy levels of water [17]. Surprisingly, however, the BODC was found to influence rotational levels with a high K_a quite strongly. These levels are notoriously difficult to treat with standard methods.

Non-adiabatic corrections to the Born–Oppenheimer approximation are much harder to determine ab initio than the adiabatic correction. Indeed, even very high quality treatments of the spectrum of H_2 do not include these completely ab initio [39]. There are quite strong indications from analysis of water spectra [15,17] that non-adiabatic corrections are important for this system. However, so far inclusion of non-adiabatic interactions, which in principle should require calculation of coupling elements involving excited electronic states, have been restricted to testing the effect of altering the mass of the nuclei in a rotation–vibration calculations.

Formally, one would expect to represent the mass of each nucleus in a nuclear motion calculation by its nuclear mass. However, the standard procedure has usually been to use atomic masses. Within a Born–Oppenheimer picture, this can be justified as the electrons instantly following the nuclei; alternatively, use of atomic masses compensates somewhat for the effects of the Born–Oppenheimer approximation [40,41]. The tests with H_2O [17] suggest that the use of a hydrogenic mass midway between the mass of atomic hydrogen and the mass of a proton gives the best results. It can be thought that a H atom electron only partially follows each H atom. A more rigorous formulation of the non-adiabatic problem for water has been given by Bunker and Moss [42], but has yet to be used in high accuracy, first principles calculations.

As far as the authors are aware, little attention has been paid to the role that relativistic motion of the electrons might have on the vibration–rotation energy levels of light molecules such as water. The recent study by Császár et al. [22] computed the relativistic effects using a first-order perturbation theory to estimate the one-electron mass–velocity and Darwin correction terms. Császár et al. found that inclusion of the relativistic correction in a calculation of the barrier to linearity of water raised the barrier height by ≈ 50 cm^{-1}. This is a significant increase in a barrier of $\approx 11\,000$ cm^{-1} and one that could have a significant effect on the nuclear motion states of the problem, particularly the band origins of the bending vibrational states. These bending band origins have in the past proved particularly troublesome [15]. Recently, Császár et al. [23] calculated a relativistic correction surface for water and found that including this effect lowered stretching excitation energies but raised bending ones. Furthermore, the relativistic correction also significantly altered rotational term values. It would appear that the relativistic correction is more significant than the adiabatic correction and may well also prove to be larger than non-adiabatic effects.

3. Method and results

3.1. Assignment procedure

In this work, the authors present many new experimental energy levels for the main $H_2{}^{16}O$ isotopomer of water. These tables of levels have been constructed as a result of a series of theoretical studies performed in conjunction with observations [9,11,43–47]. By assigning several thousand new water transitions it has been possible to build up greatly extended lists of energy levels. These tables of levels are useful in their own right, for refining theoretical techniques and potentials, and can themselves be used to make further assignments [46]. It is the authors' practice to denote assignments made in this fashion 'trivial'.

The technique developed by the authors for making non-trivial assignments relies on the use of theoretical line lists. Although some work [9,45] has exclusively used ab initio line lists, they have, in general, combined the information obtained using line lists of two types. A number of line lists have been computed using spectroscopically determined potential energy surfaces. At

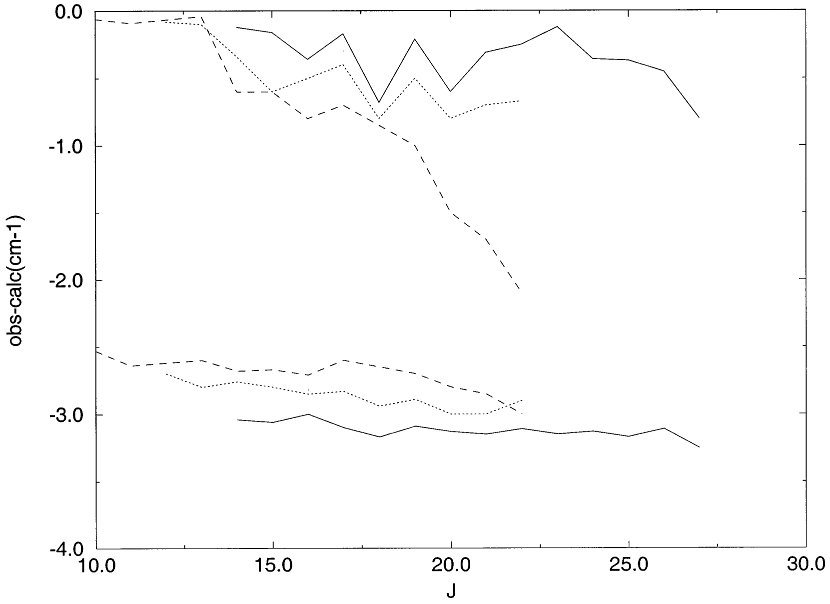

Fig. 2. Comparison of typical band errors (observed minus calculated) for the water transition in the 5000 cm^{-1} region [43]. Solid lines: (031)–(020) $K_c = J$; dotted lines: (041)–(030) $K_c = J$; dashed lines: (051)–(040) $K_c = J$. Upper three lines obtained using the PS line list [16]. The lower three lines were obtained using the authors' ab initio ZVPT line list.

present, the most accurate spectroscopic potential is due to Partidge and Schwenke [16], and either their line list (denoted PS) or a recalculation of it (denoted PSUCL) has been used. The recalculation was deemed necessary because of problems encountered at high levels of rotational excitation, J, with the original PS line list [11].

The authors ab initio linelist (denoted ZVPT) was computed using the PS ab initio Born–Oppenheimer potential energy surface supplemented by their adiabatic or BODC surface [17], and hydrogenic masses midway between atomic and nuclear. Individual transition frequencies in this line list are in general significantly less accurate than ones obtained from the PS line list, or indeed other line lists based on spectroscopic potentials. However, when used carefully, the ab initio ZVPT line list has proved to be much more powerful for making assignments.

The general technique employed here has been to follow branches of transitions through a spectrum. A branch is defined as a series of transitions for which the quantum numbers of the upper and lower states vary only according to $K_a = J - n_a$, where n_a is a constant defining a particular branch. In some cases, e.g. [43], branches defined by $K_c = J - n_c$ have also been followed.

The advantage of following a branch using the ab initio ZVPT line list is illustrated in Fig. 2. Although the absolute error on an individual transition is several wavenumbers too big to be useful for making reliable assignments by direct comparison with experimental frequencies, the change in this error on moving between neighboring members of the branch is very small. This means that it is possible to move along a branch with a high degree of confidence. Conversely, as shown in Fig. 2, a similar extrapolation using the PS line list gives much more erratic behavior. This observation is not meant as a criticism of the PS line list, as other spectroscopically determined line lists behave in a similar fashion.

The authors' assignment procedure does not only rely on following branches and transition frequencies. It is important to realise that the intensity of spectral lines also contain significant information. Transitions within a branch will generally be of a similar intensity, possibly dropping

Table 1
Energy levels with $J \geq 11$ of the (010), (020), (100) and (001) vibrational states of $H_2{}^{16}O$ in cm^{-1} derived using experimental data

J	K_a	K_c	(010)	(020)	(100)	(001)
11	0	11	2915.8756	4469.7376	4958.9040	5062.0170
11	1	11	2915.8974	4469.7966	4958.9369	5062.0201
11	1	10	3135.7662	4714.8189	5153.1911	5255.2068
11	2	10	3136.4152	4716.3795	5153.5380	5255.3471
11	2	9	3314.8569	4905.6537	5316.8024	5418.8039
11	3	9	3323.2712	4922.0901	5320.8918	5421.2683
11	3	8	3441.0401	5034.3887	5439.0578	5543.6374
11	4	8	3487.4006	5105.7299	5465.0565	5563.4005
11	4	7	3535.8705	5144.4093	5524.5720	5631.8386
11	5	7	3650.5099	5293.7910	5601.5310	5698.4892
11	5	6	3659.9043	5300.1630	5621.3344	5714.5350
11	6	6	3832.2529	5505.6230	5761.4028	5845.6548
11	6	5	3833.1455	5505.1748	5762.0569	5847.7098
11	7	5	4038.3522	5741.3914	5934.4204	6013.3672
11	7	4	4038.4041	5741.4284	5934.4788	6013.5113
11	8	4	4265.9757	5997.1774	6129.9829	6200.8931
11	8	3	4265.9783	5997.1765	6129.9860	6200.8973
11	9	3	4510.9024	6266.3730	6346.1088	6405.5196
11	9	2	4510.9024	6266.3730	6346.1088	6405.5196
11	10	2	4769.2341	6589.4166	6534.1788	6623.6695
11	10	1	4769.2341	6589.4166	6534.1788	6623.6695
11	11	1	5037.3346	6868.0766	6785.5998	6852.1681
11	11	0	5037.3346	6868.0766	6785.5998	6852.1681
12	0	12	3144.5732	4696.8432	5186.3390	5289.1539
12	1	12	3144.5794	4696.8654	5184.7374	5289.1539
12	1	11	3386.0534	4966.6331	5398.2482	5500.8581
12	2	11	3386.3820	4967.4909	5399.3354	5500.9174
12	2	10	3587.6693	5182.0949	5581.1130	5683.3357
12	3	10	3592.4256	5193.8822	5579.4922	5684.5273
12	3	9	3738.5437	5336.3271	5726.0638	5830.2594
12	4	9	3770.8807	5389.5521	5742.0311	5841.8636
12	4	8	3843.4063	5450.8894	5826.1362	5933.5463
12	5	8	3940.5200	5587.5189	5887.7684	5984.6780
12	5	7	3959.2550	5596.4250	5918.1773	6013.4512
12	6	7	4123.2858	5796.1146	6049.8488	6133.7717
12	6	6	4125.5999	5796.4534	6051.2732	6138.8915
12	7	6	4329.3255	6032.0833	6221.4271	6301.4083
12	7	5	4329.4970	6032.1969	6221.6234	6301.8717
12	8	5	4557.5459	6288.5519	6417.2977	6489.0184
12	8	4	4557.5557	6288.5509	6417.3084	6489.0398
12	9	4	4803.8230	6558.7524	6635.1119	6694.5790
12	9	3	4803.8230	6558.7524	6635.1119	6694.5801
12	10	3	5064.1416	6882.9504	6825.9003	6914.3564
12	10	2	5064.1416	6882.9504	6825.9003	6914.3564
12	11	2	5334.8635	7166.4434	7077.5814	7145.1039
12	11	1	5334.8625	7166.4434	7077.5814	7145.1039
12	12	1	5612.4881	7464.5881	7328.0698	7383.6819
12	12	0	5612.4881	7464.5881	7328.0698	7383.6819
13	0	13	3391.1305	4941.6057	5429.1259	5534.1124
13	1	13	3391.1349	4941.6224	5429.1168	5534.1124
13	1	12	3654.0504	5235.9580	5662.4779	5764.1879
13	2	12	3654.2181	5236.4325	5660.4106	5764.2082

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
13	2	11	3877.0903	5477.0064	5862.3425	5964.9135
13	3	11	3879.7199	5483.1261	5862.4642	5965.4798
13	3	10	4052.8140	5654.7613	6028.8603	6132.6529
13	4	10	4074.0401	5695.8830	6037.8728	6139.0322
13	4	9	4174.0408	5781.9585	6148.6864	6256.0207
13	5	9	4252.4444	5896.7737	6194.2882	6292.1195
13	5	8	4285.6493	5919.0089	6241.5240	6336.0457
13	6	8	4437.4014	6109.5273	6363.5721	6444.6354
13	6	7	4442.7137	6111.4681	6365.3806	6455.7455
13	7	7	4643.3815	6345.5876	6531.4792	6612.5511
13	7	6	4643.8713	6345.9102	6532.0206	6613.8339
13	8	6	4871.9499	6602.4682	6727.3189	6799.9563
13	8	5	4871.9803	6602.4633	6727.3521	6800.0525
13	9	5	5119.3751	6873.4139	6946.7019	7006.2277
13	9	4	5119.3758	6873.4139	6946.7042	7006.2426
13	10	4	5381.5559	7199.1191	7139.5926	7227.4697
13	10	3	5381.5559	7199.1191	7139.5926	7227.4697
13	11	3	5654.7811	7487.0858	7391.6763	7460.3566
13	11	2	5654.7811	7487.0858	7391.6763	7460.3566
13	12	2	5935.6018	7789.1403	7644.4468	7701.7395
13	12	1	5935.6018	7789.1403	7644.4468	7701.7395
13	13	1	6220.6220	8095.4936	7901.1968	7948.4991
13	13	0	6220.6220	8095.4936	7901.1968	7948.4991
14	0	14	3655.4858	5204.0096	5690.8784	5796.9424
14	1	14	3655.4870	5204.0202	5690.8784	5796.8933
14	1	13	3939.7477	5522.8558	5940.5421	6045.1680
14	2	13	3939.8345	5523.1220	5940.6393	6045.1410
14	2	12	4183.3919	5786.8561	6161.1265	6263.7000
14	3	12	4184.8360	5790.4345	6160.3776	6263.9245
14	3	11	4382.7831	5993.1984	6347.2902	6451.0831
14	4	11	4396.0533	6019.8342	6351.8500	6454.1276
14	4	10	4525.2385	6134.9190	6489.6188	6596.2277
14	5	10	4585.3516	6229.8947	6520.6164	6619.7838
14	5	9	4638.3524	6267.8855	6589.7465	6705.5917
14	6	9	4774.0461	6445.0840	6676.4639	6777.5338
14	6	8	4784.9961	6450.4164	6705.0302	6798.7178
14	7	8	4980.2238	6681.5933	6864.3963	6946.4675
14	7	7	4981.4710	6682.4579	6865.7317	6949.5789
14	8	7	5208.8966	6938.6234	7059.8103	7133.4845
14	8	6	5208.9941	6938.5860	7059.9348	7133.7805
14	9	6	5457.2388	7209.9926	7280.5913	7340.1823
14	9	5	5457.2446	7209.9926	7280.6011	7340.1998
14	10	5	5721.0995	7537.4854	7474.9532	7562.6758
14	10	4	5721.0995	7537.4854	7474.9532	7562.6758
14	11	4	5996.6941	7829.5439	7727.5484	7797.5472
14	11	3	5996.6941	7829.5439	7727.5484	7797.5472
14	12	3	6280.5635	8135.3191	7982.5148	8041.6093
14	12	2	6280.5635	8135.3191	7982.5148	8041.6093
14	13	2	6569.4125	8445.9957	8242.3185	8291.7857
14	13	1	6569.4125	8445.9957	8242.3185	8291.7857
14	14	1	6859.8804	8756.9768	8505.2002	8544.9484
14	14	0	6859.8804	8756.9768	8505.2002	8544.9484
15	0	15	3937.5753	5484.0001	5970.2091	6077.1101

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
15	1	15	3937.5763	5484.0087	5970.2091	6077.1101
15	1	14	4243.1121	5827.3406	6238.2150	6343.4445
15	2	14	4243.1622	5827.4860	6238.2205	6342.5294
15	2	13	4506.7354	6113.5148	6474.7070	6578.8717
15	3	13	4507.5223	6115.6576	6475.4394	6579.7438
15	3	12	4728.2242	6345.9251	6682.0054	6784.7190
15	4	12	4736.2429	6362.6404	6683.4396	6786.6850
15	4	11	4894.5909	6510.2427	6847.0956	6952.1951
15	5	11	4938.2534	6584.4154	6865.8618	6966.5832
15	5	10	5015.7064	6641.8899	6960.3902	7074.4517
15	6	10	5132.5244	6803.4061	7032.7337	7131.6294
15	6	9	5152.9671	6813.4098	7070.6346	7167.3329
15	7	9	5339.4849	7039.7445	7220.2470	7302.7162
15	7	8	5342.3488	7041.7283	7222.9552	7309.4775
15	8	8	5568.0939	7296.7762	7414.5274	7489.3038
15	8	7	5568.3556	7296.6056	7414.8615	7490.1124
15	9	7	5817.0826	7568.1446	7636.4859	7696.1598
15	9	6	5817.0983	7568.1411	7636.5057	7696.2321
15	10	6	6082.4124	7897.6037	7831.6953	7919.6522
15	10	5	6082.4124	7897.6021	7831.6953	7919.6582
15	11	5	6360.1981	8193.3607	8084.8447	8156.3070
15	11	4	6360.1981	8193.3607	8084.8447	8156.3070
15	12	4	6646.9579	8502.6506	8341.9002	8402.8805
15	12	3	6646.9579	8502.6506	8341.9002	8402.8805
15	13	3	6939.4274	8817.4380	8604.6031	8656.3080
15	13	2	6939.4274	8817.4380	8604.6031	8656.3080
15	14	2	7234.4219	9133.4117	8871.1351	8913.5595
15	14	1	7234.4219	9133.4117	8871.1351	8913.5595
15	15	1	7528.5572	9446.8428	9138.9639	9171.4740
15	15	0	7528.5572	9446.8428	9138.9639	9171.4740
16	0	16	4237.3240	5781.5167	6267.0357	6375.0580
16	1	16	4237.3245	5781.5246	6267.0357	6375.0580
16	1	15	4564.0860	6149.4112	6553.2193	6659.4486
16	2	15	4564.1140	6149.4982	6553.2200	6659.4486
16	2	14	4847.1932	6456.7867	6807.4160	6912.5747
16	3	14	4847.6264	6458.0144	6807.6671	6913.0625
16	3	13	5089.3832	6711.7041	7027.3181	7135.3199
16	4	13	5094.0873	6723.0209	7032.2315	7136.3718
16	4	12	5280.0959	6900.9986	7221.4039	7323.1139
16	5	12	5310.2453	6957.1194	7229.3014	7331.4830
16	5	11	5415.4907	7045.4384	7350.7326	7464.4845
16	6	11	5512.0169	7182.2540	7406.9557	7506.0556
16	6	10	5546.7394	7199.3142	7461.6215	7559.3903
16	7	10	5720.7221	7419.6045	7599.0901	7680.8102
16	7	9	5726.7132	7423.7545	7604.1211	7694.0249
16	8	9	5949.2187	7676.5324	7791.1870	7867.1262
16	8	8	5949.8666	7676.1620	7792.1477	7869.0342
16	9	8	6198.5735	7947.5358	8014.0521	8073.8758
16	9	7	6198.6277	7947.5755	8014.1184	8074.0529
16	10	7	6465.1281	8279.0294	8209.5240	8298.0866
16	10	6	6465.1348	8279.0353	8209.5451	8298.0911
16	11	6	6744.9006	8578.0747	8463.2281	8536.2792
16	11	5	6744.9006	8578.0886	8463.2281	8536.2792

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
16	12	5	7034.3532	8890.6670	8722.2188	8785.1582
16	12	4	7034.3532	8890.6670	8722.2188	8785.1582
16	13	4	7330.2537	9209.3409	8987.6562	9041.6391
16	13	3	7330.2537	9209.3409	8987.6562	9041.6391
16	14	3	7629.4825	9530.0093	9257.6399	9302.7547
16	14	2	7629.4825	9530.0093	9257.6399	9302.7547
16	15	2	7928.9074	9849.3364	9529.6990	9565.5098
16	15	1	7928.9074	9849.3364	9529.6990	9565.5098
16	16	1	8225.0807	10163.3651	9801.1601	9826.4935
16	16	0	8225.0807	10163.3651	9801.1601	9826.4935
17	0	17	4554.6552	6096.5254	6581.2802	6690.4736
17	1	17	4554.6555	6096.5162	6581.2802	6690.4736
17	1	16	4902.6111	6489.0558	6885.4889	6992.7655
17	2	16	4902.6230	6489.1077	6885.4889	6992.7655
17	2	15	5204.7549	6816.7592	7156.8361	7262.7993
17	3	15	5204.9945	6817.5252	7156.9121	7262.7886
17	3	14	5466.4074	7093.6411	7396.5221	7502.3851
17	4	14	5469.1980	7100.7884	7397.9722	7503.0725
17	4	13	5680.5544	7308.7714	7597.8245	7708.9576
17	5	13	5700.4824	7349.0501	7610.0614	7713.7570
17	5	12	5835.2897	7463.4019	7758.3988	7871.7219
17	6	12	5911.6309	7581.5401	7799.5862	7899.8056
17	6	11	5965.7209	7622.7292	7876.4384	
17	7	11	6123.3584	7820.6875		8076.5719
17	7	10	6134.9016	7828.5531	8009.6956	8103.5924
17	8	10	6351.8984	8077.5515	8189.5478	8266.4423
17	8	9	6353.4064	8080.5074	8191.3817	8270.6977
17	9	9	6601.3754	8347.8498	8413.1040	8472.9965
17	9	8	6601.5199	8347.9618	8413.1102	8473.5079
17	10	8	6868.8823	8681.3141	8608.2129	8697.6264
17	10	7	6868.8920	8681.3283	8608.2274	8697.6730
17	11	7	7150.4090	8983.3161	8862.3407	8937.1156
17	11	6	7150.4090	8983.2906	8862.3407	8937.1270
17	12	6	7442.3418	9298.9133	9123.1029	9188.0588
17	12	5	7442.3418	9298.9105	9123.1029	9188.0588
17	13	5	7741.4362	9621.2321	9391.0768	9447.3675
17	13	4	7741.4362	9621.2321	9391.0768	9447.3675
17	14	4	8044.6542	9946.3018	9664.3096	9712.1009
17	14	3	8044.6542	9946.3018	9664.3096	9712.1009
17	15	3	8348.9761	10271.1167	9940.3546	9979.3958
17	15	2	8348.9761	10271.1167	9940.3546	9979.3958
17	16	2	8651.2796	10591.8103	10216.6274	10245.9139
17	16	1	8651.2796	10591.8103	10216.6274	10245.9139
17	17	1	8947.9974	10905.0417	10490.4623	10508.8639
17	17	0	8947.9974	10905.0417	10490.4623	10508.8639
18	0	18	4889.4911	6428.9656	6912.8492	7023.2862
18	1	18	4889.4912	6428.9656	6912.8492	7023.2862
18	1	17	5258.6278	6846.2472	7234.9675	7343.3431
18	2	17	5258.6339	6846.2811	7234.9682	7343.3431
18	2	16	5579.3641	7193.5257	7523.1400	7630.0138
18	3	16	5579.4979	7193.9715	7523.1637	7630.0070
18	3	15	5859.6295	7490.9946		7885.9283
18	4	15	5861.2438	7495.4721	7780.4012	7885.7999

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
18	4	14	6095.5206	7730.6706		8110.0953
18	5	14	6108.2857	7758.7880	8008.1168	8112.8429
18	5	13	6272.7581	7904.2263		8294.0906
18	6	13	6330.4536	8000.3494	8210.2962	8311.9435
18	6	12	6408.3994	8057.7284		8433.9711
18	7	12	6546.7278	8242.3947	8394.9631	8496.4016
18	7	11	6567.2825	8256.0940	8439.8614	8537.6588
18	8	11	6775.7903	8499.2998	8609.3611	8686.8686
18	8	10	6778.9182	8502.2826	8613.1770	8695.4047
18	9	10	7025.1592	8768.7428	8832.8434	8893.2154
18	9	9	7025.4750	8769.0715	8833.2127	8894.3411
18	10	9	7293.3109	9103.4400	9027.4359	9118.0045
18	10	8	7293.3350		9027.4787	9118.0785
18	11	8	7576.3351	9408.5525	9281.8987	9358.4622
18	11	7	7576.3395	9408.5269	9281.9023	9358.4636
18	12	7	7870.5116	9726.9427	9544.1688	9611.2213
18	12	6	7870.5116	9726.9484	9544.1688	9611.2213
18	13	6	8172.5647	10052.6499	9814.4826	9873.0925
18	13	5	8172.5647	10052.6499	9814.4826	9873.0925
18	14	5	8479.4860	10381.8270	10090.7344	10141.1836
18	14	4	8479.4860	10381.8270	10090.7344	10141.1836
18	15	4	8788.3806	10711.7491	10370.5211	10412.7077
18	15	3	8788.3806	10711.7491	10370.5211	10412.7077
18	16	3	9096.2919	11038.5633	10651.3159	10684.3531
18	16	2	9096.2919	11038.5633	10651.3159	10684.3531
18	17	2	9400.0666	11359.4698	10930.5363	10953.8310
18	17	1	9400.0666	11359.4698	10930.5363	10953.8310
18	18	1	9695.9599	11670.5244	11205.5980	11217.1595
18	18	0	9695.9599	11670.5244	11205.5980	11217.1595
19	0	19	5241.7443	6778.7944	7261.6567	7373.3923
19	1	19	5241.7443	6778.7944	7261.6567	7373.3923
19	1	18	5632.0440	7220.9682	7601.5495	7711.0935
19	2	18	5632.0475	7221.4700	7601.5495	7711.0935
19	2	17	5970.9360	7586.9210	7906.1717	8014.1080
19	3	17	5971.0105	7587.2098	7906.1657	8014.1120
19	3	16	6269.0682	7903.9287	8179.0337	8286.0005
19	4	16	6270.0257	7906.7298		8286.0190
19	4	15	6525.0604	8166.5883		8526.6918
19	5	15	6533.0697	8185.6424		8529.1683
19	5	14	6725.8668	8361.9494	8618.8560	8730.6290
19	6	14	6767.5943	8437.8379		8741.6050
19	6	13	6873.0019	8517.2624		8887.1020
19	7	13	6990.0636	8684.0687		8934.8419
19	7	12	7023.9820	8706.3124	8894.1854	8994.5647
19	8	12	7219.8900	8941.4025	9050.5884	9127.7049
19	8	11	7226.5028	8946.0943	9057.3071	9143.4871
19	9	11	7469.5488	9210.2474	9273.4423	9334.1471
19	9	10	7470.3064	9210.7011	9274.1444	9336.6316
19	10	10	7738.0347	9546.7846	9466.9364	9558.7802
19	10	9	7738.1310	9546.7799	9467.0329	9559.0572
19	11	9	8022.2884		9721.5120	9799.9477
19	11	8	8022.3010	9853.3791	9721.5309	9800.0080
19	12	8	8318.4627	10174.3218	9985.1097	10054.2588

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
19	12	7	8318.4627	10174.3231	9985.1097	10054.2588
19	13	7	8623.2229	10503.1550	10257.4768	10318.4520
19	13	6	8623.2229	10503.1550	10257.4768	10318.4520
19	14	6	8933.5676	10836.1350	10536.5269	10589.5994
19	14	5	8933.5676	10836.1350	10536.5269	10589.5994
19	15	5	9246.6901	11170.7951	10819.7890	10865.0418
19	15	4	9246.6901	11170.7951	10819.7890	10865.0418
19	16	4	9559.7880	11503.2479	11104.8162	11141.4185
19	16	3	9559.7880	11503.2479	11104.8162	11141.4185
19	17	3	9869.9305	11831.0944	11389.0967	11416.8746
19	17	2	9869.9305	11831.0944	11389.0967	11416.8746
19	18	2	10173.9005	12150.9157	11670.0865	11687.6774
19	18	1	10173.9005	12150.9157	11670.0865	11687.6774
19	19	1	10467.7137	12458.5783	11945.3599	11950.2228
19	19	0	10467.7137	12458.5783	11945.3599	11950.2228
20	0	20	5611.3316	7145.9818	7627.5854	7740.6869
20	1	20	5611.3316	7145.9818	7627.5854	7740.6869
20	1	19	6022.7991	7613.1933	7985.1341	8095.9007
20	2	19	6022.8011	7613.1861	7985.1341	8095.9007
20	2	18	6379.3494	7996.8930	8305.9434	8414.9724
20	3	18	6379.3953	7997.0053	8305.9448	8414.9724
20	3	17	6694.7583	8332.5150		8702.3755
20	4	17	6695.3045	8334.2686	8594.8029	8702.4598
20	4	16	6969.4103	8616.1261		8958.9851
20	5	16	6974.3710	8628.6039		8959.4612
20	5	15	7193.2373	8835.5834		9181.2181
20	6	15	7222.2619	8893.1128	9083.0558	
20	6	14	7357.0562			9357.7249
20	7	14	7452.5345	9144.9699	9290.5848	9391.3359
20	7	13	7504.5739	9178.1900		9471.0034
20	8	13	7685.1160	9403.2930		9588.3134
20	8	12	7696.2859			9615.1323
20	9	12	7934.1732	9671.4988	9733.8425	9795.3484
20	9	11	7935.7681	9672.7046		9800.3387
20	10	11	8202.7527	10009.0683	9926.4600	10019.7505
20	10	10	8202.9301	10009.2258		10020.3609
20	11	10	8487.9064	10317.4473	10180.8922	10261.2574
20	11	9	8487.9038	10317.4178	10180.9317	10261.3216
20	12	9	8785.7937	10640.5862	10445.5241	10516.8381
20	12	8	8785.7915		10445.5164	10516.8292
20	13	8	9092.9950	10972.2869	10719.7419	10783.0390
20	13	7	9092.9950	10972.3052	10719.7419	10783.0390
20	14	7	9406.5167	11308.7915	11001.2864	11056.9821
20	14	6	9406.4863	11308.7915	11001.2864	11056.9821
20	15	6	9723.5132	11647.8249	11287.7734	11335.9997
20	15	5	9723.5132	11647.8249	11287.7734	11335.9997
20	16	5	10041.3653	11985.4702	11576.7243	11616.7332
20	16	4	10041.3653	11985.4702	11576.7243	11616.7332
20	17	4	10357.3407	12319.6327	11865.7288	11897.6519
20	17	3	10357.3407	12319.6327	11865.7288	11897.6519
20	18	3	10668.4944	12647.2621	12152.3131	12175.2222
20	18	2	10668.4944	12647.2621	12152.3131	12175.2222
20	19	2	10971.5087	12964.8911	12433.9908	12446.2965

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
20	19	1	10971.5087	12964.8911	12433.9908	12446.2965
20	20	1	11262.0879	13268.0600	12708.6137	12706.9600
20	20	0	11262.0879	13268.0600	12708.6137	12706.9600
21	0	21	5998.1662	7530.5090	8010.5330	8125.0614
21	1	21	5998.1662	7530.5090	8010.5330	8125.0614
21	1	20	6430.7999	8022.9973	8385.6027	8497.6618
21	2	20	6430.5969		8385.6027	8497.6618
21	2	19	6804.4792	8423.0140	8722.2532	8832.4823
21	3	19	6804.4764		8722.2727	8832.4823
21	3	18	7136.5844	8776.7436		9135.1168
21	4	18	7136.9306			9135.0886
21	4	17	7428.7624	9080.8947		9406.9283
21	5	17	7431.8085			9407.2263
21	5	16	7674.1401	9323.2255	9535.8210	9646.4481
21	6	16	7693.7284			9649.2141
21	6	15	7858.3879	9502.8572		
21	7	15	7933.3031			9865.2872
21	7	14	8007.8846	9676.6015		
21	8	14	8169.3693			10068.0475
21	8	13	8188.7182	9898.4281		10109.6195
21	9	13	8418.2025			10276.3693
21	9	12	8421.7651	10155.0223		10285.7095
21	10	12	8687.0416		10405.6893	10500.4435
21	10	11	8687.4369		10406.1682	10501.8060
21	11	11	8972.7940			10742.0369
21	11	10	8972.8389	10800.2302	10659.8313	10742.2068
21	12	10	9272.0919	11125.3497	10925.0887	10998.4975
21	12	9	9272.1200	11125.5382	10925.0769	10998.5151
21	13	9	9581.4759		11200.8058	11266.4726
21	13	8	9581.4892	11459.6319	11200.8058	11266.5135
21	14	8	9897.8624	11799.3648	11484.6903	11542.9492
21	14	7	9897.5771	11799.3621	11484.6903	11542.9260
21	15	7	10218.4659	12142.4182	11774.0743	11825.2208
21	15	6	10218.4498	12142.4182	11774.0743	11825.2208
21	16	6	10540.6701	12484.8332	12066.6810	12109.9239
21	16	5	10540.6701	12484.8332	12066.6810	12109.9239
21	17	5	10861.9485	12824.7758	12360.0390	12395.8345
21	17	4	10861.9485	12824.7758	12360.0390	12395.8345
21	18	4	11179.6053	13159.4127	12651.8386	12679.5271
21	18	3	11179.6053	13159.4127	12651.8386	12679.5271
21	19	3	11490.6769	13485.7650	12939.6358	12958.2209
21	19	2	11490.6769	13485.7650	12939.6358	12958.2209
21	20	2	11791.6989	13800.2256	13221.0186	13228.5624
21	20	1	11791.6989	13800.2256	13221.0186	13228.5624
21	21	1	12077.9849	14097.9093	13494.2916	13486.3986
21	21	0	12077.9849	14097.9093	13494.2916	13486.3986
22	0	22	6402.1559	7932.5404	8410.3833	8526.4026
22	1	22	6402.1559	7932.5617	8410.3833	8526.4026
22	1	21	6855.9610		8802.8504	8916.2546
22	2	21	6855.9621	8450.0090	8802.8504	8916.2546
22	2	20	7246.1300		9154.9992	9266.4796
22	3	20	7246.1810	8865.2187	9154.9992	9266.4796
22	3	19	7594.4977			9583.9070

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
22	4	19	7594.6903	9237.2929		
22	4	18	7902.9990			9870.5114
22	5	18	7904.8618	9564.0419		
22	5	17	8168.4122			10125.5173
22	6	17	8181.3646	9853.8307	10020.7949	
22	6	16	8374.9731			
22	7	16	8431.5264			
22	7	15	8532.5068			
22	8	15	8672.4647		10465.3646	
22	8	14	8703.7634			
22	9	14	8922.5107			10776.3237
22	9	13	8928.2750			10793.1152
22	10	13	9190.5203		10904.1843	11000.5580
22	10	12	9191.3075			11003.3449
22	11	12	9476.5907		11157.6233	11241.9328
22	11	11	9476.7605		11157.7852	11242.2983
22	12	11	9777.0289	11628.1669	11423.4302	11499.0104
22	12	10	9777.0671			11499.0321
22	13	10	10088.2753	11964.8124	11700.5003	11768.4013
22	13	9	10088.2775	11964.7537	11700.5003	11768.4065
22	14	9	10407.2559	12307.4007	11986.3197	12047.0767
22	14	8	10407.5423		11986.3197	12047.0463
22	15	8	10731.0987	12654.1509	12278.3748	12332.2974
22	15	7	10731.0961	12654.1509	12278.3748	12332.2939
22	16	7	11057.3211	13000.9386	12574.2441	12620.6927
22	16	6	11057.3211	13000.9386	12574.2441	12620.6927
22	17	6	11383.4404	13346.1477	12871.6801	12911.0556
22	17	5	11383.4404	13346.1477	12871.6801	12911.0556
22	18	5	11706.9661	13687.1323	13168.2812	13200.3356
22	18	4	11706.9661	13687.1323	13168.2812	13200.3356
22	19	4	12025.2409	14021.2358	13461.7860	13485.8461
22	19	3	12025.2409	14021.2358	13461.7860	13485.8461
22	20	3	12335.2572	14345.3987	13749.7872	13764.7093
22	20	2	12335.2572	14345.3987	13749.7872	13764.7093
22	21	2	12633.3482	14655.8284	14029.9845	14033.4184
22	21	1	12633.3482	14655.8284	14029.9845	14033.4184
22	22	1	12914.3736	14947.1329	14301.3932	14287.5580
22	22	0	12914.3736	14947.1329	14301.3932	14287.5580
23	0	23	6823.2165	8350.9655	8827.0219	8944.5858
23	1	23	6823.2165	8350.9706	8827.0219	8944.5858
23	1	22	7298.2141	8894.6928	9236.7512	9351.5577
23	2	22	7298.2118	8894.6642	9236.7512	9351.5577
23	2	21	7704.2283	9323.1442	9603.9985	9716.8329
23	3	21	7704.2359		9604.0146	9716.8329
23	3	20	8068.3018	9711.7354		
23	4	20	8068.4359			10048.7874
23	4	19	8393.2846	10050.6989		
23	5	19	8394.4419			10349.6652
23	5	18	8676.2688	10337.0159	10509.6220	
23	6	18	8684.6366			
23	6	17	8905.1796	10557.0767		
23	7	17	8946.4154			
23	7	16	9076.1120			

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
23	8	16	9193.6082			
23	8	15	9241.1846			
23	9	15	9445.1785			.6800
23	9	14	9455.4065			
23	10	14	9710.8967			11519.6401
23	10	13	9714.4903			11524.6847
23	11	13	9998.8308			11760.6516
23	11	12	9999.1524		11674.6264	11761.3879
23	12	12	10300.1580		11940.2584	12017.9389
23	12	11	10300.2308		11940.3160	12018.0359
23	13	11	10612.9585		12218.4649	12288.4565
23	13	10	10613.0326	12487.2207	12218.3278	12288.4781
23	14	10	10934.2636	12832.5345	12505.8347	12568.9703
23	14	9	10933.9501	12832.5191	12505.8347	12568.9703
23	15	9	11261.0630	13182.5831	12800.2566	12856.8586
23	15	8	11261.0729	13182.5831	12800.2566	12856.8586
23	16	8	11590.9374	13533.3594	13099.1573	13148.5246
23	16	7	11590.9374	13533.3594	13099.1573	13148.5246
23	17	7	11921.4762	13883.4114	13400.2485	13443.1317
23	17	6	11921.4762	13883.4114	13400.2485	13443.1317
23	18	6	12250.3206	14230.1423	13701.3070	13737.3226
23	18	5	12250.3206	14230.1423	13701.3070	13737.3226
23	19	5	12575.0668	14571.1869	14000.0569	14029.0012
23	19	4	12575.0668	14571.1869	14000.0569	14029.0012
23	20	4	12892.9887	14903.8615	14294.2593	14315.4250
23	20	3	12892.9887	14903.8615	14294.2593	14315.4250
23	21	3	13201.0587	15225.0309	14581.5423	14593.5873
23	21	2	13201.0587	15225.0309	14581.5423	14593.5873
23	22	2	13495.3971	15530.6740	14859.7399	14859.8845
23	22	1	13495.3971	15530.6740	14859.7399	14859.8845
23	23	1	13770.2797	15814.7806	15128.9817	15109.5728
23	23	0	13770.2797	15814.7806	15128.9817	15109.5728
24	0	24	7261.2908	8787.4668	9260.3218	9379.4932
24	1	24	7261.2908	8787.4668	9260.3218	9379.4932
24	1	23	7757.4718		9687.1742	9803.4415
24	2	23	7757.4718	9356.8173	9687.1742	9803.4415
24	2	22	8178.4015		10069.1140	10183.3502
24	3	22	8178.4126	9796.2185	10069.1095	10183.3502
24	3	21	8557.8682			10529.4340
24	4	21	8557.9466			
24	4	20	8897.8567			
24	5	20	8898.5777			
24	5	19	9197.7388			
24	6	19	9203.1773		11020.4512	
24	6	18	9448.1082			
24	7	18	9477.2013			
24	7	17	9636.6427			11585.6265
24	8	17	9732.0986			
24	8	16	9801.8355			
24	9	16	9986.0849			
24	9	15	10003.2839			
24	10	15	10253.8827			
24	10	14	10256.6605			

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
24	11	14	10539.1565			12297.5288
24	11	13	10539.8117			12299.2807
24	12	13	10841.0744		12475.1780	12554.9993
24	12	12	10841.1957			12555.2103
24	13	12	11154.9785		12754.0062	12826.2463
24	13	11	11155.3175		12754.0062	12826.3236
24	14	11	11478.5588	13374.2727	13042.9579	13108.3673
24	14	10	11478.3228		13042.9579	13108.3643
24	15	10	11807.9788	13727.3222	13339.3810	13398.5733
24	15	9	11807.9551	13727.3222	13339.3810	13398.5733
24	16	9	12141.1441		13640.9903	13693.2773
24	16	8	12141.1441		13640.9903	13693.2773
24	17	8	12475.6966	14436.1858	13945.4361	13991.4329
24	17	7	12475.6966	14436.1858	13945.4361	13991.4329
24	18	7	12809.3593	14788.1318	14250.5344	14290.3302
24	18	6	12809.3593	14788.1318	14250.5344	14290.3302
24	19	6	13139.9174	15135.4164	14554.1414	14587.4272
24	19	5	13139.9174	15135.4164	14554.1414	14587.4272
24	20	5	13464.8867	15475.6446	14854.0371	14880.5878
24	20	4	13464.8867	15475.6446	14854.0371	14880.5878
24	21	4	13781.6440	15806.1157	15148.0097	15167.0739
24	21	3	13781.6440	15806.1157	15148.0097	15167.0739
24	22	3	14087.0039	16123.5921	15433.7178	15443.8104
24	22	2	14087.0039	16123.5921	15433.7178	15443.8104
24	23	2	14376.8473	16423.7897	15709.1722	15707.0297
24	23	1	14376.8473	16423.7897	15709.1722	15707.0297
24	24	1	14644.7826	16699.9777	15976.1988	15951.7021
24	24	0	14644.7826	16699.9777	15976.1988	15951.7021
25	0	25	7715.6676	9241.1757	9710.1587	9830.9896
25	1	25	7715.6676	9241.1757	9710.1587	9830.9896
25	1	24	8233.6459	9836.4492	10154.0013	10271.7747
25	2	24	8233.6459		10154.0013	10271.7747
25	2	23	8668.3810		10550.1160	10665.8616
25	3	23	8668.4992		10550.2746	10665.8616
25	3	22	9062.9792			
25	4	22	9063.0981			11025.7344
25	4	21	9417.4836			
25	5	21	9417.9523			11352.2296
25	5	20	9732.9852			
25	6	20	9736.4353			
25	7	19	10023.3026			
25	7	18	10212.1228			
25	8	18	10287.0269			
25	8	17	10380.0643			
25	9	17	10544.4752			
25	9	16	10572.0911			
25	10	16	10812.6017			12612.6430
25	10	15	10817.7236			
25	11	15	11098.4116			
25	11	14	11098.5726			
25	12	14	11398.7523			13109.8387
25	12	13	11399.7929			13110.0094
25	13	13	11715.7324			

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
25	13	12	11714.7658		13307.0369	
25	14	12	12039.6874		13597.1855	13664.8200
25	14	11	12039.4769		13597.1855	13664.7924
25	15	11	12371.4385			13956.9685
25	15	10	12371.4475	14287.9416	13895.4798	13956.9685
25	16	10	12707.5623	14645.9766	14199.4217	14254.3825
25	16	9	12707.5617	14645.9586	14199.4217	14254.3825
25	17	9	13045.7453		14506.8908	14556.0257
25	17	8	13045.7453		14506.8908	14556.0257
25	18	8	13384.1366	15360.7438	14815.6792	14858.8134
25	18	7	13384.1366	15360.7438	14815.6792	14858.8134
25	19	7	13719.5985	15713.6449	15123.6772	15161.0191
25	19	6	13719.5985	15713.6449	15123.6772	15161.0191
25	20	6	14050.8575	16060.6048	15428.8300	15460.0869
25	20	5	14050.8575	16060.6048	15428.8300	15460.0869
25	21	5	14375.2494	16399.2636	15728.9477	15753.9020
25	21	4	14375.2494	16399.2636	15728.9477	15753.9020
25	22	4	14690.0709	16726.8800	16021.8366	16039.7161
25	22	3	14690.0709	16726.8800	16021.8366	16039.7161
25	23	3	14992.0293	17040.0632	16305.1802	16314.3818
25	23	2	14992.0293	17040.0632	16305.1802	16314.3818
25	24	2	15276.7459	17334.2413	16577.1959	16574.0008
25	24	1	15276.7459	17334.2413	16577.1959	16574.0008
25	25	1	15537.0109	17601.8800	16842.2078	16813.2538
25	25	0	15537.0109	17601.8800	16842.2078	16813.2538
26	0	26	8187.6896	9712.1038	10176.4007	10298.9460
26	1	26	8187.6896	9712.1038	10176.4007	10298.9460
26	1	25	8726.6643	10333.8761	10637.0990	10756.4203
26	2	25	8726.6643	10333.9082	10637.0990	10756.4203
26	2	24	9174.2422		11046.8655	11164.1618
26	3	24	9174.3061		11046.8232	11164.1618
26	3	23				11537.5031
26	4	23	9583.3521			
26	4	22	9951.9142			
26	5	22	9952.2255			
26	5	21	10281.5849			
26	6	21	10283.8026			
26	6	20	10570.5259			
26	8	19	10857.7630			
26	8	18	10978.1504			
26	9	18	11120.1338			
26	9	17	11161.5299			
26	10	17	11388.8768			
26	10	16	11397.7006			
26	11	16	11673.7929			
26	11	15	11674.8400			
26	12	15	11976.4725			
26	12	14	11975.5080			
26	13	14	12291.4192			13953.5056
26	13	13	12290.9413			13953.8898
26	14	13	12617.2674		14168.1526	
26	14	12	12616.9735			
26	15	12	12951.0490		14468.0633	14531.6269

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
26	15	11	12951.1530		14468.0633	14531.6700
26	16	11	13289.8161	15224.9593	14774.1689	14831.5100
26	16	10	13289.8161		14774.1689	14831.5100
26	17	10	13631.2594	15586.7226	15084.2748	15136.1963
26	17	9	13631.2594	15586.7226	15084.2748	15136.1963
26	18	9	13973.3834		15396.3935	15442.8112
26	18	8	13973.3834		15396.3935	15442.8112
26	19	8	14313.8221	16305.4250	15708.4043	15749.2713
26	19	7	14313.8221	16305.4250	15708.4043	15749.2713
26	20	7	14650.7260	16657.7889	16018.2979	16053.8586
26	20	6	14650.7260	16657.7889	16018.2979	16053.8586
26	21	6	14981.8931	17004.9707	16324.0346	16354.0638
26	21	5	14981.8931	17004.9707	16324.0346	16354.0638
26	22	5	15304.9597	17341.0682	16623.5303	16647.7970
26	22	4	15304.9597	17341.0682	16623.5303	16647.7970
26	23	4	15617.1851	17665.1103	16914.5963	16932.2940
26	23	3	15617.1851	17665.1103	16914.5963	16932.2940
26	24	3	15915.1550	17973.4569	17194.8379	17204.3429
26	24	2	15915.1550	17973.4569	17194.8379	17204.3429
26	25	2	16194.1849	18261.1715	17462.7505	17459.9184
26	25	1	16194.1849	18261.1715	17462.7505	17459.9184
26	26	1	16446.1297	18519.6823	17726.2300	17693.5938
26	26	0	16446.1297	18519.6823	17726.2300	17693.5938
27	0	27	8676.1124	10200.6934	10658.9126	10783.2199
27	1	27	8676.1124	10200.6934	10658.9126	10783.2199
27	1	26	9236.4755	10855.0631	11136.3239	11257.2285
27	2	26	9236.4755		11136.3239	11257.2285
27	2	25	9695.3656		11559.0332	11678.0127
27	3	25	9695.3250		11559.0755	11678.0127
27	3	24	10119.1434			
27	4	24				12064.4907
27	4	23	10500.9068			
27	5	23	10501.2190			12418.4215
27	5	22	10837.7789			
27	6	22	10838.5007			
27	7	21	11159.0360			
27	7	20	11401.7133			
27	9	19	11711.8457			
27	9	18	11774.7944			
27	10	18	11982.2103			
27	10	17	11996.6845			
27	11	17	12266.4911			
27	11	16	12268.8650			
27	12	16	12568.1359			
27	12	15	12568.0056			
27	13	15	12884.1603			
27	14	14	13211.1478			14827.6242
27	14	13	13210.7748			14827.4536
27	15	12			15056.7285	
27	16	12	13887.5739		15364.7997	15424.3000
27	16	11	13887.5187		15364.7997	15424.3000
27	17	11	14231.8602	16183.5684		15731.6800
27	17	10	14231.8602	16183.5684	15677.2898	15731.6800

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
27	18	10	14577.5808	16548.1712	15992.3758	16041.6477
27	18	9	14577.5808	16548.1712	15992.3758	16041.6477
27	19	9	14922.2848		16307.9899	16352.2576
27	19	8	14922.2848		16307.9899	16352.2576
27	20	8	15264.2639		16622.2229	16661.4486
27	20	7	15264.2639	17270.6073	16622.2229	16661.4486
27	21	7	15601.4781		16933.0961	16967.5714
27	21	6	15601.4781		16933.0961	16967.5714
27	22	6	15931.8072	17966.1879	17238.6034	17268.1629
27	22	5	15931.8072	17966.1879	17238.6034	17268.1629
27	23	5	16252.8926	18299.6307	17536.7128	17561.1604
27	23	4	16252.8926	18299.6307	17536.7128	17561.1604
27	24	4	16561.9472	18169.7380	17825.1951	17843.7771
27	24	3	16561.9472	18169.7380	17825.1951	17843.7771
27	25	3	16855.4098	18922.8757	18101.6479	18112.7555
27	25	2	16855.4098	18922.8757	18101.6479	18112.7555
27	26	2	17128.2919	19203.6937	18364.8145	18363.9987
27	26	1	17128.2919	19203.6937	18364.8145	18363.9987
27	27	1	17371.3456	19452.6140	18627.5700	18592.1868
27	27	0	17371.3456	19452.6140	18627.5700	18592.1868
28	0	28	9181.1450	10706.9474	11157.5604	11283.6730
28	1	28	9181.1450	10706.9474	11157.5604	11283.6730
28	1	27	9763.1973		11651.5407	11774.0444
28	2	27	9763.1973		11651.5407	11774.0444
28	2	26	10231.3286		12086.6126	12207.1869
28	3	26	10231.3833		12086.6126	12207.1869
28	3	25				12606.6017
28	4	25	10669.6086			
28	4	24	11064.2378			
28	5	24	11063.7952			
28	5	23	11424.8572			
28	8	21	12043.5515			
28	10	18	12614.6461			
28	11	18	12876.1203			
28	11	17	12880.0426			
28	12	17	13176.7404			
28	12	16	13176.9979			
28	13	16	13492.7621			
28	13	15	13492.3870			
28	14	14	13820.1562			
28	15	14	14157.3799			
28	15	13	14157.1713			15729.2733
28	17	12	14847.1503			16342.1300
28	17	11	14847.1911			16342.1300
28	18	11	15196.1557		16603.3927	
28	18	10	15196.1557			
28	19	10	15544.6773		16922.1754	16969.3277
28	19	9	15544.6773		16922.1754	16969.3277
28	20	9	15891.1979		17240.2830	17282.9698
28	20	8	15891.1979		17240.2830	17282.9698
28	21	8	16233.8186	18251.6338	17555.8099	17594.0255
28	21	7	16233.8186		17555.8099	17594.0255
28	22	7	16570.5932		17866.8236	17900.9210

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
28	22	6	16570.5932		17866.8236	17900.9210
28	23	6	16899.4370	18943.9608	18171.3104	18201.2296
28	23	5	16899.4370	18943.9608	18171.3104	18201.2296
28	24	5	17217.9658	19274.0699	18467.3528	18492.9251
28	24	4	17217.9658	19274.0699	18467.3528	18492.9251
28	25	4	17523.3823	19589.7815	18752.5971	18773.1981
28	25	3	17523.3823	19589.7815	18752.5971	18773.1981
28	26	3	17811.8653	19887.3011	19024.6253	19038.6918
28	26	2	17811.8653	19887.3011	19024.6253	19038.6918
28	27	2	18078.2267	20160.9011	19282.4164	19285.4501
28	27	1	18078.2267	20160.9011	19282.4164	19285.4501
28	28	1	18311.8937	20399.9338	19545.5800	19508.5037
28	28	0	18311.8937	20399.9338	19545.5800	19508.5037
29	0	29	9702.7316	11231.0719	11672.2740	11800.1525
29	1	29	9702.7316	11231.0719	11672.2740	11800.1525
29	1	28	10312.8367		12182.6094	12306.7531
29	2	28	10312.9457		12182.6094	12306.7531
29	2	27	10781.9300		12629.2675	12751.5419
29	3	27	10781.9300		12629.2675	12751.5419
29	3	26	11234.8515			
29	4	26				13163.5754
29	4	25	11641.6093			
29	5	25	11641.4147			
29	6	24	12015.4766			
29	11	19	13501.4910			
29	12	18	13801.7569			
29	12	17	13802.2231			
29	13	17	14117.4539			
29	13	16	14116.8565			
29	14	16	14445.5431			
29	14	15	14444.9228			
29	15	15	14783.2971			
29	16	14	15127.8641			
29	16	13	15127.9333			
29	18	12	15828.8188			17282.7600
29	18	11	15828.8188			17282.7600
29	19	11	16180.6712			
29	19	10	16180.6712			
29	20	10	16531.2237		17872.2100	
29	20	9	16531.2237		17872.2100	
29	21	9	16878.6118			
29	21	8	16878.6118			
29	22	8	17220.8819			
29	22	7	17220.8819			
29	23	7	17557.1822			
29	23	6	17557.1822			
29	24	6	17883.6977	19937.0315		
29	24	5	17883.6977	19937.0315		
29	25	5	18199.1403	20263.3295		
29	25	4	18199.1403	20263.3295		
29	26	4	18500.3783	20574.2813		19719.4591
29	26	3	18500.3783	20574.2813		19719.4591
29	27	3	18783.6177	20865.9597		

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
29	27	2	18783.6177	20865.9597		
29	28	2	19043.1723	21132.7703		
29	28	1	19043.1723	21132.7703		
29	29	1	19267.0405	21360.9139		
29	29	0	19267.0405	21360.9139		
30	0	30	10240.8158	11773.3137	12202.4062	12332.5123
30	1	30	10240.8158	11773.3137	12202.4062	12332.5123
30	1	29	10863.9022			12855.1790
30	2	29	10863.9022			12855.1790
30	2	28	11346.6595		13186.8900	13310.9758
30	3	28	11346.6595		13186.8900	13310.9758
30	3	27				13735.1905
30	4	27	11814.7383			
30	5	26	12232.9152			
30	7	23				15113.7885
30	12	18	14443.1436			
30	13	18	14757.1847			
30	13	17	14756.6591			
30	14	17	15085.4262			
30	14	16	15084.6052			
30	15	16	15423.9715			
30	15	15	15424.1306			
30	17	14	16120.4923			
30	19	12	16829.9179			
30	19	11	16829.9179			
30	20	11	17183.9756			
30	20	10	17183.9756			
30	21	10	17535.1688			
30	21	9	17535.1688			
30	22	9	17884.2409			
30	22	8	17884.2409			
30	24	7	18559.3634			
30	24	6	18559.3634			
30	25	6	18883.4346			
30	25	5	18883.4346			
30	26	5	19195.4100			
30	26	4	19195.4100			
30	27	4	19492.3293			
30	27	3	19492.3293			
30	28	3	19769.7304	21857.9365		
30	28	2	19769.7304	21857.9356		
30	29	2	20022.3369			
30	29	1	20022.3369			
30	30	1	20236.0800	22334.8803		
30	30	0	20236.0800	22334.8803		
31	0	31	10795.3528			
31	1	31	10795.3528			
31	1	30	11439.9132			
31	2	30	11439.9132			13419.1899
31	2	29	11925.6136			
31	3	9	11925.6136			13885.3491
31	3	8	12408.8999			
31	4	7	12836.7065			

Table 1 (continued)

J	K_a	K_c	(010)	(020)	(100)	(001)
31	13	19	15411.9549			
31	14	17	15738.8959			
31	15	16	16079.9095			
31	28	4	20497.9165			
31	28	3	20497.9165			
31	30	2	21014.9405			
31	30	1	21014.9405			
31	31	1	21218.3900			13998.5730
31	31	0	21218.3900			
33	31	2	22020.3000			
33	31	1	22020.3000			

somewhat at higher J. How this information has been used varies according to the temperature and type of spectrum. For example, the unassigned N-window (750–1010 cm^{-1}) sunspot spectrum was split into four echelons on intensity grounds. So far, only the strongest two echelons have been analyzed. Conversely, analyses of laboratory spectra have generally attempted to assign lines of all intensities.

Water spectra analyzed so far in this fashion include: the spectrum of sunspots ($T \approx 3200$ K) in the 750–1010 cm^{-1} region [9,11] and 4600–5100 cm^{-1} region [43]. Laboratory spectra of hot water in the 370–930 cm^{-1} region ($T \approx 1800$ K) [9,11,45], 900–2000 cm^{-1} region with $T \approx 1250$ K [44] and very recently $T \approx 1800$ K [47]. Finally, the authors have recently analyzed a room temperature near IR (13 200–16 500 cm^{-1}) spectrum [44]. Analysis of other water spectra, both hot and room temperature, is currently in progress.

Finally, it should be noted that Schwenke [24] has also developed methods of assigning water spectra using line lists. His method, which uses the PS linelist, like the current one, uses both frequency and intensity information. PS used an automatic procedure to assign a complete set of quantum number labels to each energy level. Analysis by the authors [11,43] suggests that these labels must be treated with caution, particularly for highly excited levels.

Schwenke's method of assignment [24] is more computer automated than the authors, which means that a large quantity of data can be processed relatively easily. However, the method does not appear to use combination differences or similar cross-checking to eliminate errors, and is therefore, more prone to yield misassignments. Furthermore these assignments use the PS labels, which means that many transitions are incorrectly labeled. To the authors' knowledge, use of this method has been restricted to analyzing room temperature water spectra.

3.2. Energy levels

In completed studies so far [9,11,43,44,46], the authors have assigned over 5000 new water transitions. Where appropriate, these assignments have been published alongside the associated experimental work. A very compact method of representing the large amount of information obtained from these studies is via stacks of experimental energy levels relative to the (000) 0_{00} ground state. By combining data from the various analyses, it has been possible to build up very extensive sets of energy levels. It is these that are presented here.

Tables 1 and 2 give measured energy for bands of water within the $n = 1$ and $n = 2$ polyads, respectively. Corresponding tables for the vibrational ground state (000) (the $n = 0$ polyad), the (240), (042), (320), (170), (071), (122), (330), (311), (033), (410) and (113) states, which belong to the $n = 4$ polyad, have been presented elsewhere [11,47]. The results in Tables 1 and 2 are only given for $J > 10$, as for the lower lying levels most of these states are well-known from earlier studies [8,44,48–51]; in the case of (040), the low J data is given in Table 3.

Table 2
Energy levels with $J \geq 11$ of the (030), (110), (011) and (040) vibrational states of $H_2{}^{16}O$ in cm^{-1} derived using experimental data

J	K_a	K_c	(030)	(110)	(011)	(040)
11	0	11	5986.3290	6530.5773	6631.1740	7462.0360
11	1	11	5986.5340	6530.7925	6631.1753	7462.9077
11	1	10	6260.4320	6746.7961	6845.7838	7769.5707
11	2	10	6264.4678		6846.1095	7780.6625
11	2	9	6459.4570	6924.1588	7023.2234	7970.4591
11	3	9	6491.7907		7028.2962	
11	3	8	6592.1870	7050.5678	7152.4460	8114.7702
11	4	8	6700.1018		7185.8523	8273.1941
11	4	7	6727.9390	7141.4909	7236.8850	8292.0259
11	5	7	6917.3066	7258.1283	7339.5174	8539.0553
11	5	6	6923.7900	7263.0842	7351.9316	8535.2343
11	6	6	7166.8305		7508.7506	8819.6509
11	6	5	7168.0966	7431.3849	7510.0965	8820.1441
11	7	5	7434.8767		7700.5128	
11	7	4	7434.9021	7632.4116	7700.5935	9122.1746
11	8	4	7719.5873	7858.5325	7912.9126	
11	8	3	7719.5873	7858.5325	7912.9170	9433.9977
11	9	3	8010.1973	8110.0498	8141.8734	
11	9	2	8010.1973	8110.0498	8141.8734	
11	10	2	8392.1575	8293.3837	8383.6022	
11	10	1	8392.1575	8293.3837	8383.6022	
11	11	1	8698.8726	8567.6605	8634.5125	
11	11	0	8698.8726	8567.6605	8634.5125	
12	0	12	6212.5320		6856.2792	7688.5747
12	1	12	6212.6550	6753.1384	6856.2792	7689.1644
12	1	11	6515.3640		7091.8276	8030.3162
12	2	11	6517.8120	6996.5781	7091.9557	8037.6605
12	2	10	6742.1831		7290.6279	
12	3	10	6767.3028		7293.2653	8313.0025
12	3	9	6897.1012		7443.8814	8419.6789
12	4	9	6982.1245	7369.6204	7465.7658	8570.1331
12	4	8	7030.8805		7554.2972	8589.0169
12	5	8	7213.3541	7531.1333	7626.5448	8825.7688
12	5	7	7216.6057		7650.3486	8824.5366
12	6	7	7456.8074	7717.8121	7797.2443	9108.5948
12	6	6	7461.0358		7800.6496	
12	7	6	7725.0484	7919.4292	7988.9411	9411.4900
12	7	5	7725.0962		7989.2141	
12	8	5	8010.5006		8201.8245	9723.7400
12	8	4	8010.5006		8201.8405	
12	9	4	8301.5255	8401.0951	8432.0830	
12	9	3	8301.5255	8401.0951	8432.0840	
12	10	3	8687.6828		8675.7942	
12	10	2	8687.6828		8675.7942	
12	11	2	8998.7345	8860.4211	8929.3751	
12	11	1	8998.7345	8860.4211	8929.3751	
12	12	1	9320.0216	9135.8203	9189.3443	
12	12	0	9320.0216	9135.8203	9189.3443	
13	0	13	6456.2957	6995.8565	7099.0256	7932.6951
13	1	13	6456.3792		7098.9992	7933.1071
13	1	12	6787.6530	7256.2687	7355.3842	8308.2325
13	2	12	6789.1198		7355.3811	8313.0908
13	2	11	7043.8360	7475.6198	7574.6523	8571.2049

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
13	3	11	7058.4226		7575.9123	
13	3	10	7221.1845		7751.3463	8745.8571
13	4	10	7293.7811		7764.8755	8870.5886
13	4	9	7359.4727	7780.8097	7878.2122	8911.5101
13	5	9	7523.0035		7935.0250	
13	5	8	7534.4331	7879.5608	7975.2009	
13	6	8	7769.3448		8108.4897	
13	6	7	7760.1161	8032.4070	8116.1153	9422.8410
13	7	7	8037.8229		8300.2348	
13	7	6	8037.9573	8229.6498	8301.0255	
13	8	6	8323.7014		8513.3689	
13	8	5	8323.7014	8457.3786	8513.4018	
13	9	5	8614.8939		8744.6999	
13	9	4	8614.8939	8714.5301	8744.7030	
13	10	4	9005.4227	8898.0847	8990.2504	
13	10	3	9005.4227	8898.0847	8990.2504	
13	11	3	9320.6112	9175.1632	9246.3587	
13	11	2	9320.6112	9175.1632	9246.3587	
13	12	2	9646.1724	9453.1665	9509.5980	
13	12	1	9646.1724	9453.1665	9509.5980	
13	13	1	9974.3555	9733.2029	9776.5818	
13	13	0	9974.3555	9733.2029	9776.5818	
14	0	14	6717.6156		7358.5296	8194.4926
14	1	14	6717.6665	7255.2584	7356.7482	8194.7828
14	1	13	7077.4166		7636.8023	
14	2	13	7078.3120	7534.3346	7636.3686	8606.8488
14	2	12			7875.8587	
14	3	12	7369.3717	7775.0916	7875.9916	8919.7205
14	3	11	7567.3201		8074.2115	
14	4	11	7618.5745		8082.2487	9192.0565
14	4	10	7711.6344		8222.8415	
14	5	10	7855.0373		8263.9719	9470.5337
14	5	9	7877.4762		8324.3539	
14	6	9	8103.8511	8361.4694	8441.8662	9752.7703
14	6	8			8457.1036	
14	7	8	8372.5727		8634.0877	
14	7	7	8372.5538		8636.0491	
14	8	7	8658.8090	8790.2101	8847.2418	
14	8	6		8790.3614	8847.4081	
14	9	6	8949.9530	9049.9585	9079.3941	
14	9	5	8949.9530		9079.3991	
14	10	5	9344.9000	9233.0696	9326.5805	
14	10	4	9344.9000	9233.0696	9326.5805	
14	11	4	9663.9980	9511.5182	9585.0761	
14	11	3	9663.9980	9511.5182	9585.0761	
14	12	3	9993.6631	9792.0720	9851.4362	
14	12	2	9993.6631	9792.0720	9851.4362	
14	13	2			10122.3486	
14	13	1			10122.3486	
14	14	1	10658.1201	10359.9213	10394.4410	
14	14	0	10658.1201	10359.9213	10394.4410	
15	0	15	6996.4870	7531.8400	7636.6179	8474.0820
15	1	15	6996.5095		7636.6179	8474.2592

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
15	1	14	7384.7880	7831.7351	7934.0518	8916.7142
15	2	14	7385.3374		7935.8141	
15	2	13	7690.7511	8101.1638	8191.8128	9231.8573
15	3	13	7696.8667		8193.3623	
15	3	12	7924.3479		8412.5303	9463.2922
15	4	12	7964.2644		8417.2456	
15	4	11	8079.3748	8488.5869	8584.5856	
15	5	11	8210.2324		8612.4504	
15	5	10	8245.2951	8597.8976	8694.2103	
15	6	10	8460.1007		8796.5828	
15	6	9	8455.8649		8823.8967	
15	7	9	8729.1953		8990.0820	
15	7	8	8730.5710	8918.2940	8994.5045	10411.3077
15	8	8			9203.1637	
15	8	7	9015.6043		9203.6034	
15	9	7		9407.0619	9435.8286	
15	9	6	9306.3476	9407.0619	9435.8404	
15	10	6		9589.3460	9684.4260	
15	10	5		9589.3460	9684.4260	
15	11	5	10028.2689	9869.0954	9945.1119	
15	11	4	10028.2689	9869.0954	9945.1119	
15	12	4	10361.9649	10151.9826	10214.4099	
15	12	3	10361.9649	10151.9826	10214.4099	
15	13	3	10699.7514	10438.5695	10489.0583	
15	13	2	10699.7514	10438.5695	10489.0583	
15	14	2	11035.5637	10726.9945	10765.8651	
15	14	1	11035.5637	10726.9945	10765.8651	
15	15	1		11014.9784		
15	15	0		11014.9784		
16	0	16	7292.9125		7931.6864	8771.4593
16	1	16	7292.9268	7825.7302	7931.6864	8771.6764
16	1	15	7709.8458		8249.9545	
16	2	15	7710.2013		8249.9545	9249.2782
16	2	14	8038.1342		8526.9882	9584.5008
16	3	14	8042.0507	8425.5290	8528.0554	9597.1094
16	3	13	8300.0450		8766.5425	
16	4	13	8326.8708		8769.4098	9907.0828
16	4	12	8485.3831		8961.5694	
16	5	12	8583.0976		8979.4818	
16	5	11	8634.8578		9106.5386	
16	6	11	8837.4429		9171.8301	
16	6	10			9216.0095	
16	7	10	9107.1747		9367.6787	
16	7	9	9110.0413		9376.6522	
16	8	9	9393.4327	9521.1297	9580.7539	
16	8	8	9393.6896		9581.8644	
16	9	8	9683.7865		9813.6928	
16	9	7			9813.7780	
16	10	7	10087.2467	9966.5701	10063.4245	
16	10	6	10087.2467	9966.5701	10063.4245	
16	11	6		10247.5139	10326.0616	
16	11	5		10247.5139	10326.0616	
16	12	5		10532.6254	10598.0811	

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
16	12	4		10532.6254	10598.0811	
16	13	4	11092.6429	10822.1715	10876.2446	
16	13	3	11092.6429	10822.1715	10876.2446	
16	14	3	11433.3283	11114.4327	11157.4901	
16	14	2	11433.3283	11114.4327	11157.4901	
16	15	2	11774.0068	11406.9019		
16	15	1	11774.0068	11406.9019		
17	0	17	7606.8652	8136.8338	8244.0177	9087.0234
17	1	17			8244.0177	
17	1	16	8052.6757		8582.9462	9597.1381
17	2	16	8052.8710		8582.9462	
17	2	15	8401.6401		8878.5512	9951.8992
17	3	15	8404.1583		8877.6521	
17	3	14	8688.6860		9136.5851	10242.8191
17	4	14			9138.5616	
17	4	13	8899.1853	9232.8126	9353.0593	
17	5	13			9364.2833	
17	5	12	9067.0830			
17	6	12	9235.1970		9566.6621	
17	6	11	9271.5824		9631.7278	
17	7	11			9766.2643	
17	8	10			9979.7059	
17	8	9	9792.8422		9983.2971	
17	9	9			10212.6470	
17	9	8	10081.9914	10184.1348	10212.9207	
17	10	8			10463.1924	
17	10	7	10489.0474	10364.3714	10463.2304	
17	11	7	10818.3180	10646.3945	10727.5394	
17	11	6	10818.3180	10646.3945	10727.5410	
17	12	6		10933.5513	11002.0473	
17	12	5		10933.5513	11002.0473	
17	13	5		11225.9057	11283.4872	
17	13	4		11225.9057	11283.4872	
17	14	4		11521.6523	11568.8603	
17	14	3		11521.6523	11568.8603	
17	15	3		11818.5047		
17	15	2		11818.5047		
17	16	2	12536.2362			
17	16	1	12536.2362			
18	0	18			8573.5549	
18	1	18	7938.4967	8465.0855	8573.5549	9421.5678
18	1	17			8933.1199	
18	2	17	8413.4425		8933.1199	9965.3847
18	2	16			9246.8664	
18	3	16	8782.8887		9246.7414	
18	3	15			9522.6532	
18	4	15	9105.1039			
18	4	14			9759.0548	
18	5	14	9385.4831		9766.1593	
18	5	13			9944.8018	
18	6	13	9652.5842			
18	6	12			10068.1404	
18	7	12	9925.1840			

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
18	7	11			10215.1038	
18	8	11			10399.5244	
18	8	10			10404.5222	
18	9	10			10632.3085	
18	9	9			10632.9325	
18	10	9	10910.7107	10782.5002		
18	10	8			10883.4310	
18	11	8	11242.7381	11065.2446	11149.1415	
18	11	7			11149.1515	
18	12	7	11586.7510	11354.3593	11425.9804	
18	12	6	11586.7238	11354.3593	11425.9804	
18	13	6		11649.3099	11710.4522	
18	13	5		11649.3099	11710.4522	
18	14	5		11948.3620	11999.5471	
18	14	4		11948.3620	11999.5471	
18	15	4		12249.1968		
18	15	3		12249.1968		
18	16	3		12549.4197		
18	16	2		12549.4197		
18	17	2	13322.2882			
18	17	1	13322.2882			
19	0	19	8287.7366		8920.2198	
19	1	19	8287.7704		8920.2198	
19	1	18	8791.8794		9300.4117	
19	2	18	8791.9316		9300.4117	
19	2	17	9176.6499		9631.8066	
19	3	17			9631.8130	
19	3	16	9509.9242			
19	4	16			9924.2594	
19	4	15	9765.5322		10179.7675	
19	5	15			10185.0123	
19	5	14	9961.7199			
19	6	14			10412.0361	
19	6	13	10145.0258			
19	8	12			10839.6069	
19	9	10			11073.7001	
19	10	10			11323.6653	
19	11	9			11590.5276	
19	11	8	11686.2866		11590.5470	
19	12	8			11869.2151	
19	12	7	12033.1696	11794.5434	11869.2151	
19	13	7	12386.4509	12091.9784	12156.4884	
19	13	6	12386.4492	12091.9784	12156.4884	
19	14	6		12394.0816	12449.3251	
19	14	5		12394.0816	12449.3251	
19	15	5		12698.6900		
19	15	4		12698.6900		
19	16	4		13003.4000		
19	16	3		13003.4000		
19	17	3		13305.7854		
19	17	2		13305.7854		
19	18	2	14130.7932			
19	18	1	14130.7932			

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
20	0	20			9283.9254	
20	1	20	8655.2101		9283.9254	
20	1	19			9684.7359	
20	2	19	9188.3346		9684.7359	
20	2	18			10033.3768	
20	3	18	9588.2586		10033.3810	
20	3	17			10343.1978	
20	4	17	9948.2584			
20	4	16			10615.4660	
20	5	16	10259.3176			
20	6	15	10542.9876			
20	7	14	10822.0066			
20	9	11			11535.0248	
20	10	10			11783.9583	
20	11	9			12051.2968	
20	12	9	12498.0553		12331.6262	
20	12	8			12331.6262	
20	13	8	12854.5284	12553.3872		
20	14	7		12858.4109		
20	14	6		12858.4109		
20	15	6		13166.5053		
20	15	5		13166.5053		
20	16	5		13475.4323		
20	16	4		13475.4323		
20	18	3		14086.2470		
20	18	2		14086.2470		
20	19	2	14960.5265			
20	19	1	14960.5265			
21	0	21	9038.8311		9664.5815	
21	1	21	9038.9206		9664.5815	
21	1	20	9602.7172		10086.0235	
21	2	20			10086.0235	
21	2	19			10451.2882	
21	3	19			10451.2882	
21	4	18			10777.4622	
21	5	17			11066.4821	
21	11	11			12531.0212	
21	12	10			12812.6689	
21	12	9			12812.6147	
21	13	8	13340.2514			
21	14	7		13340.8318		
21	15	7		13652.2473		
21	15	6		13652.2473		
21	19	3		14889.4800		
21	19	2		14889.4800		
21	20	2	15810.3585			
21	20	1	15810.3585			
22	0	22			10062.0943	
22	1	22	9441.8785		10062.0943	
22	1	21			10504.1613	
22	2	21	10035.5222		10504.1613	
22	2	20			10885.3219	
22	3	20	10454.4857		10885.3219	

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
22	4	18			11532.0848	
22	15	8		14155.4044		
22	20	3		15714.2550		
22	20	2		15714.2550		
22	21	2	16679.2326			
22	21	1	16679.2326			
23	0	23			10476.3764	
23	1	23			10476.3764	
23	1	22			10939.1425	
23	2	22			10939.1425	
23	2	21			11335.1521	
23	3	21			11335.1521	
23	21	3		16559.3500		
23	21	2		16559.3500		
23	22	2	17566.1606			
23	22	1	17566.1606			
24	0	24			10907.3492	
24	1	24			10907.3492	
24	1	23			11390.7998	
24	2	23			11390.7998	
24	2	22			11800.4057	
24	3	22			11800.4057	
24	5	19			12807.2114	
24	22	3		17423.6100		
24	22	2		17423.6100		
24	23	2	18470.2016			
24	23	1	18470.2016			
25	1	25			11356.4842	
25	1	24			11859.0623	
25	2	24			11859.0623	
25	2	23			12281.0790	
25	3	23			12281.0790	
25	24	2	19390.4582			
25	24	1	19390.4582			
26	0	26			11818.7249	
26	1	26			11818.7249	
26	1	25			12343.9225	
26	2	25			12343.9225	
26	2	24			12777.7600	
26	3	24			12777.7600	
26	25	2	20326.0796			
26	25	1	20326.0796			
27	0	27			12299.1181	
27	1	27			12299.1181	
27	1	26			12845.2356	
27	2	26			12845.2356	
27	26	2	21276.2322			
27	26	1	21276.2322			
28	0	28			12795.9086	
28	1	28			12795.9086	
28	1	27			13363.0732	
28	2	27			13363.0732	
28	27	2	22240.0464			

Table 2 (continued)

J	K_a	K_c	(030)	(110)	(011)	(040)
28	27	1	22240.0464			
29	0	29			13309.3334	
29	1	29			13309.3334	
29	1	28			13897.1421	
29	2	28			13897.1421	
30	0	30			13837.6484	
30	1	30			13837.6484	

Table 3 presents energy levels for the (040), (050) and (060) vibrational states. The (040) data complements that given in Table 2, although there are some duplications for completeness, and extends the data given previously [51,44]. The (050) and (060) levels have been substantially derived from very recent analysis of a laboratory emission spectrum of hot water [47], augmented by some information obtained from other studies that have found transitions involving these levels [43,44]. There are no previous experimental data on these levels available. Indeed, it is only relatively recently that it has been shown that the widely accepted values for the band origins of these states were in error [44].

Tables 1 and 2 are notably complete; this work greatly extends information on states with high K_a, which were particularly poorly characterized in earlier works. Several of the highest K_a levels are analyzed below. Tabulations of energy levels are particularly useful for making so-called trivial assignments in other spectral regions (a technique already employed by the authors [46]).

However, a word of warning is necessary. Measured transition frequencies are the true fundamental data characterizing the water spectrum and any interpretation of this data, e.g. to give energy levels, must be treated with due caution. This is particularly true of data derived from assignment of the pure rotational spectrum in sunspots. In this case, many of the newly derived energy levels are based on a single transition. There are two problems here. First, stacks of such transitions are subject to accumulation of experimental errors, and therefore suffer from some loss of accuracy. Second and more seriously, while being confident about these assignments, misassignments are possible. A single misassignment can lead to a large number of erroneous energy levels. To help mitigate these problems, combination differences have been used where ever possible to confirm the energy levels. Short wavelength spectra are more helpful in this respect than pure rotational spectra for a number of reasons. First, high-lying levels can be linked directly to the ground state for which stacks of energy levels are well-known [11,46]. Second, a complete vibration–rotation spectrum will include a number of transitions involving any individual upper state, meaning that energies and assignments can be confirmed using combination differences. However, such spectra are not always available, and in any case, bending overtones are usually too weak to measure.

By combining assignments from different spectra it is possible to specify levels that have been obtained more than once by independent analysis. These levels can be treated with complete confidence. In work on the pure rotational spectrum of hot water in the sunspot and laboratory [9,11], the authors obtained energy levels from observed transition frequencies that are significantly higher in K_a and energy than any known previously. However, these levels were obtained from only one frequency for each level, which makes them vulnerable for the possible misassignments.

The authors' work on the bending fundamental and overtones, the $(0v_20)$ states, [44] allowed them to assign transitions to levels with energies and K_a values lower than those in the pure rotational spectrum, but still significantly higher than any in the available literature. Since many transitions in the bending manifold involved common upper

Table 3
Energy levels of the (040), (050) and (060) vibrational states of $H_2{}^{16}O$ in cm^{-1} derived using experimental data

J	K_a	K_c	(040)	(050)	(060)
1	0	1	6157.7557	7566.0181	
1	1	0	6201.0727	7629.0847	
2	2	1	6359.0504	7828.7321	9271.2848
2	2	0	6359.7830	7829.2465	
3	0	3	6272.6297	7681.3007	
3	1	2	6334.8967	7763.1182	9139.0803
3	2	1	6434.1927	7902.8849	9344.3695
3	3	0	6604.3800	8122.4395	9628.7838
4	1	4	6378.5610	7805.6307	
4	2	3	6525.2990	7995.2119	
4	2	2	6535.4565	8002.5058	
4	3	2	6701.4797	8219.4331	9725.7492
4	3	1	6701.8844	8219.6746	
4	4	1	6919.9370	8486.1856	10049.2887
5	0	5	6466.5150	7878.5498	9210.1555
5	1	5	6478.7994	7905.8179	
5	1	4	6570.0650	7999.9585	9377.2305
5	2	3	6664.3530	8129.1232	9565.5203
5	3	3	6822.8600	8340.5737	
5	3	2	6824.4200	8341.4847	9847.2309
5	4	2	7041.9540	8608.1979	
5	4	1	7041.9830	8608.2554	10717.2956
5	5	1	7295.4940	8906.9324	
5	5	0	7295.4940	8906.9324	
6	0	6	6589.7437	8004.4853	
6	1	6	6597.7317	8025.1116	9400.8270
6	2	5	6781.5000	8252.8282	
6	3	4	6968.2170	8485.6176	
6	3	3	6972.6082	8488.1469	
6	4	3	7188.2520	8754.1788	
6	5	2	7442.3420	9054.2858	10666.2502
6	6	1	7722.6145	9374.3336	
6	6	0	7722.6145	9374.3336	
7	0	7	6729.8970	8147.5873	9487.9474
7	1	7	6734.9800	8162.7223	
7	1	6	6895.8580	8331.6697	9714.7601
7	2	6	6941.6355	8414.4204	
7	2	5	7003.9180	8463.4181	
7	3	5	7137.0885	8654.1238	
7	3	4	7147.2140	8660.1249	
7	4	3	7359.6140	8924.6117	
7	5	2	7613.3810	9226.1805	10837.7055
7	6	2	7894.7640	9546.5498	
7	6	1	7894.7640	9546.5498	
7	7	1	8193.6609	9879.8429	
7	7	0	8193.6609	9879.8429	
8	1	8	6890.2700	8318.6761	9697.2265
8	2	7	7122.1890	8597.2149	
8	3	6	7328.8810	8845.5585	
8	4	5	7552.9770	9117.2873	
8	5	4	7807.1463	9421.2236	
8	6	3	8090.8128	9742.4816	
8	6	2		9742.4816	
9	0	9	7061.3780	8484.7530	9838.3104
9	1	9	7063.4214	8492.8427	
9	1	8	7298.5760	8747.3527	10143.7006
9	2	7	7444.1260	8901.0704	
9	3	6	7577.8640	9081.8098	10574.3208
9	4	5	7775.6380	9336.7483	
9	5	4	8027.0275	9645.8165	
9	6	3	8310.5620	9961.8429	
10	0	10	7253.0009	8678.9886	
10	1	10	7254.3206	8685.0994	10069.1994
10	2	9	7542.1480	9023.9954	10483.2847
10	3	8	7778.0022	9293.6852	
10	4	7	8011.3226	9570.5494	
11	0	11	7462.0360	8890.7719	10259.4559
11	1	11	7462.9077	8895.2138	
11	1	10	7769.5707	9236.6458	10656.5126
11	2	9	7970.4591	9430.4767	
11	3	8	8114.7702	9607.1423	
11	4	7	8292.0259	9844.3278	
12	1	12	7689.1644	9123.5710	10518.0688
12	2	11	8037.6605	9529.8446	
12	3	10	8313.0025	9832.6338	
13	0	13	7932.6951	9367.3807	10756.2926
13	1	12	8308.2325	9795.5300	
14	1	14	8194.7828	9635.0166	11043.9614
14	2	13	8606.8488	10112.9912	
15	0	15	8474.0820	9917.0305	
15	1	14	8916.7142	10425.2703	
16	1	16	8771.6764	10222.7611	
16	2	15	9249.2782	10773.1715	

states, the levels derived from this analysis can be regarded as completely reliable within statistical errors. In particular, the levels up to $K_a = 19$ for the (010) state, $K_a = 16$ for the (020) state and $K_a = 14$ for (030) state can be regarded as secure. These already greatly extend previously published values.

4. Discussion

The results presented in this work comprise many new energy levels for water that have been compiled as a result of analysis by the authors of a series of water spectra. This analysis has already found a number of unanticipated features of the

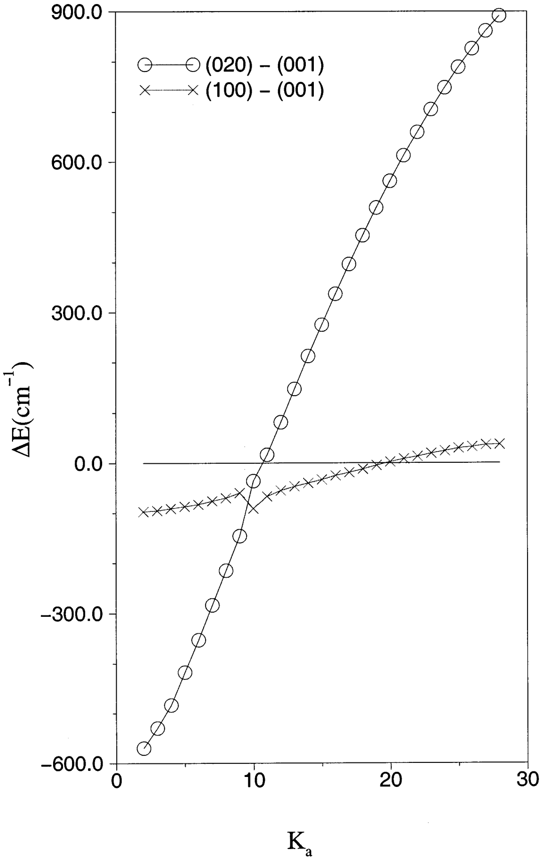

Fig. 3. Energy levels of states with $K_a = J$ as a function of J for the (001), (020) and (001) vibrational states. For each value of J, the zero of energy is taken as the J_{J0} level of the (001) state.

water spectrum; in particular, the discovery of rotational difference bands have been discussed elsewhere [9,45].

Analysis of the structure of the energy levels themselves also contains interesting information. Fig. 3 plots J_{J0} levels of the (020) and (100) vibrational states relative to those of the (001) state as function of J. Note that the J_{J1} levels are essentially degenerate with those shown. Prior to our work, there had been considerable difficulty in assigning transitions involving these states for $J > 9$ [45]. It is clear from the figure that this difficulty is associated with the avoided crossings in this region. It is the interactions caused by the avoided crossings that give rise to the rotational difference bands that are found for all states with $K_a \approx 10$. Such interactions, which arise from Coriolis coupling, are included naturally in variational calculations based on the use of exact nuclear motion kinetic energy operators.

There has been considerable recent interest in the phenomenon of clustering of rotationally excited states in H_2X systems. These clusters manifest themselves as fourfold (quasi)-degenerate levels forming instead of the usual twofold degeneracies found for any asymmetric top at high J in the rigid rotor model. Two types of clustering have been identified [52]. Type I clustering occurs for the vibrational ground state and has been observed experimentally for H_2Se [53]. It is now well-established that water does not display Type I clusters [14,54].

Type II clustering can only occur with pairs of vibrationally excited states, such as the (100) and (001) stretching fundamentals. Again Type II clustering has been observed in H_2Se [55]. The situation in the case of water is given in Fig. 3. For $J = 14–19$ it would appear that the J_{J0} and J_{J1} levels of the (100) and (001) states are approaching each other asymptotically as would be expected for clustering behavior. It was at this point that the previous analysis stopped [45]. However, plotting the full set of levels now available show that for $J = 20$, the rotational levels cross each other and continue to separate.

This means that it can now be definitively said that water does not show Type II clustering either.

Fig. 4 gives another representation of the J_{J0} states of water. In this case, the levels depicted are those associated with bending mode excitation. The figure uses assigned bending overtone levels up to the (060) state [47] with higher levels, which are yet to be observed, taken from the authors ZVPT first principles calculations. To aid visualization, levels with $J > 0$ have been reflected about the $J = 0$ axis and have also shown for $J < 0$. Data has been given in this fashion to illustrate the profound influence the barrier to linearity is expected to have on the spectrum of water.

The $v_2 = 10$ state is the first bending overtone that should sample linear regions of the potential. Recent semi-classical and quantal analysis by Child and co-workers [56,57] suggests that this

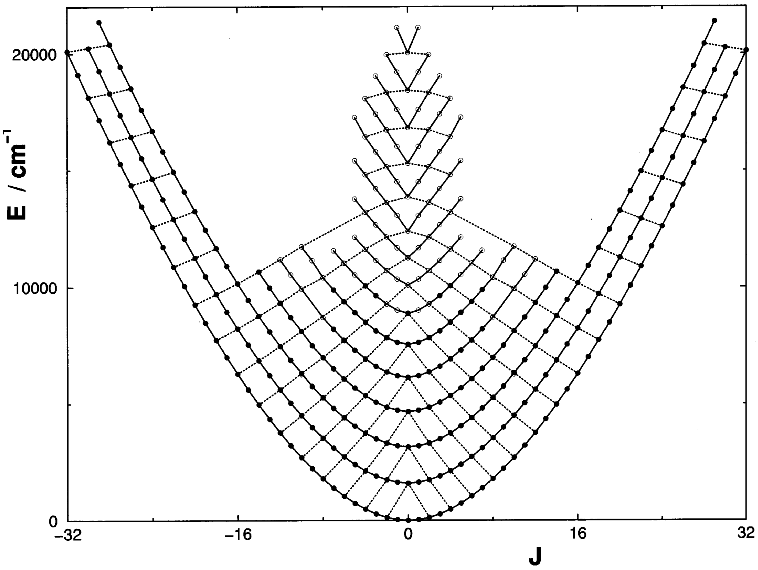

Fig. 4. Energy levels of states $(0v_20)$ with $K_a = J$. Experimentally determined levels are closed dots and those from the ZVPT linelist are open dots. The lines have been drawn to illustrate the change in the behavior about the monodromy point, which appears to the (080) 0_{00} level, see text for details. Levels plotted for negative J are simply a reflection of the positive J ones.

point on the potential, known as the monodromy point, will strongly influence how the levels should be assigned. The solid lines in the figure join levels with the same bending quantum number, v_2. Dashed lines join levels with the same 'linear molecule' quantum number $n = 2v_2 + K_a$. The interesting point is to note how the slopes of these lines behave at $J = 0$. As shown by the data, there is a sharp change in this behavior at about the $v_2 = 8$ 0_{00} level, which the results suggest should be the monodromy point.

So far there is insufficient assigned experimental data on the higher bending states of water to confirm that water does indeed show the generic behavior associated with quantum monodromy. However, over 80% of the experimentally determined levels plotted in Fig. 4 have come from the authors' recent assignments. They are confident that continued work on the water molecule will bring us to the situation where the idea of quantum monodromy can be empirically tested.

5. Conclusion

First principles calculations of the spectrum of water has led to a significant increase in the range and complexity of spectra that are amenable to theoretical analysis. By assigning water spectra, the authors have been able to construct greatly extended tables of measured energy levels. This extension is in the number of measured levels, the range of energies they cover, and in the vibrational and rotational states for which levels are available.

Clearly this situation is highly satisfactory. However, there is still much to be done. For example, an analysis of the spectrum of sunspots in the 750–1010 cm^{-1} region has led to the assignment of 1657 new transitions [9,11]. However, these represent only about 15% of the well-resolved and reproducible lines in this spectrum. The great majority of the remaining unassigned lines must also belong to water, probably in higher states not yet studied. Analyzing this spectrum, and others that remain unassigned in the literature [2], will probably require further refinements to the theoretical procedures discussed in this article.

Another way of looking at this problem is to consider the energy levels of water. Prior to the authors' work, just over 4000 water energy levels had been experimentally determined. This number has been approximately doubled. Theoretical line list calculations have computed energies for up to about 200 000 levels [16,30]. A recently completed first principles calculation of the partition function and related thermodynamic properties of water at high temperature, had to supplement these levels with more, even higher energy ones [58]. This suggests that hot ($T > 3000$ K) environments such as sunspots, 'cool' stars and flames, where water spectra can be recorded, may well contain information on a very large number of water levels. There is undoubtedly still a number of important challenges ahead in the theoretical spectroscopy of water.

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