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Band Origins for Water up to 22 000 cm^{-1}: A Comparison of Spectroscopically Determined Potential Energy Surfaces

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Rovibrational energy levels are calculated for water using four potential energy surfaces recently determined from spectroscopic data. By using Radau coordinates and a discrete variable representation of the angular coordinate the lowest 172 band origins are converged to 0.1 cm^{-1} or better. These results are compared to the 62 observed band origins for $H_2{}^{16}O$. Comparisons are also made for the $J = 1$ and $J = 2$ term values for the lowest 10 vibrational states. The best potential, due to Jensen (*J. Mol. Spectrosc.* **133**, 438 (1989)), reproduces the observed band origins with a standard deviation of 6.4 cm^{-1} and 0.10 cm^{-1} for the term values. This potential shows a small systematic error in that it overestimates many higher band origins. Estimates are given for all the unobserved band origins below 22 000 cm^{-1}. © 1991 Academic Press, Inc.

1. INTRODUCTION

The variational calculation of vibrational energy levels has now become a standard technique for triatomic molecules (*1–3*). This has led to a number of workers using variational calculations to construct potential energy surfaces for chemically bound triatomic systems including H_2O (*4–7*), H_2S and H_2Se (*5, 7*), and HCN (*8*).

In this technique one makes an initial guess for the potential, usually an appropriate functional form with parameters that can be optimized. The function is then improved by successive recalculation of observed transition frequencies until a satisfactory level of convergence is reached. Because high resolution spectroscopic data carry a wealth of information about the potential, this method is capable of yielding global potential energy surfaces to high accuracy. Furthermore, unlike perturbation theory based force constant representations which define the potential to high order at a single (equilibrium) geometry, these global surfaces are a useful starting point for further studies on the system in question. Thus, for example, a surface fitted to a set of vibrational band origins can be used to predict not only other vibrational band origins, but also rotationally excited levels of the system.

Fitting potential energy surfaces in this fashion is computationally expensive because many recalculations of the observed data are usually required. For example, Jensen's surface required 200–300 h on a powerful mainframe computer (*6*). For this reason the fits represent a compromise between the accuracy of the variational calculation used in the fitting procedure and the complexity, as represented by the number of free parameters, of the potential function used. The latter may be constrained by the availability of data although this has not been so for water where none of the quoted fits used all the available experimental data.

In performing these calculations there are three areas in which approximation may occur:

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TABLE I

Comparison of Observed and Calculated Band Origins for Symmetric Vibrational States of Water

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
0 1 0	0 0^+ 1	1594.7	−0.7	−0.4	+1.0	+0.4
0 2 0	0 0^+ 2	3151.6	−0.4	+0.1	+2.8	−0.4
1 0 0	1 0^+ 0	3657.1	+0.7	−0.1	−3.7	+0.6
0 3 0	0 0^+ 3	4666.8	+1.3	+0.3	+3.9	−0.9
1 1 0	1 0^+ 1	5235.0	+0.5	+1.0	−0.9	+0.7
0 4 0	0 0^+ 4	6134.0	+4.8	−1.5	+2.7	−0.2
1 2 0	1 0^+ 2	6775.1	+3.1	+3.3	+4.8	+0.0
2 0 0	2 0^+ 0	7201.5	−2.9	−2.2	−8.3	−1.2
0 0 2	1 1^+ 0	7445.1	+2.4	+1.2	+3.5	+0.1
0 5 0	0 0^+ 5		7531.5	7551.0	7545.8	7539.9
1 3 0	1 0^+ 3	8274.0	+7.4	+5.5	+12.3	+0.7
2 1 0	2 0^+ 1	8761.6	−2.5	+0.2	−5.6	−1.4
0 6 0	0 0^+ 6		8850.0	8898.9	8889.3	8863.3
0 1 2	1 1^+ 1	9000.1	+2.5	−0.4	−3.0	−2.1
1 4 0	1 0^+ 4		9711.8	9719.8	9703.5	9719.9
0 7 0	0 0^+ 7		10054.1	10161.0	10131.7	10073.9
2 2 0	2 0^+ 2	10284.4	+3.0	+4.1	+2.4	−1.5
0 2 2	1 1^+ 2	10524.3	+6.7	+4.7	−2.5	−1.4
3 0 0	3 0^+ 0	10599.7	−8.8	−4.8	−8.1	−3.2
1 0 2	2 1^+ 0	10868.9	+11.9	−4.3	−2.0	−0.5
1 5 0	1 0^+ 5		11087.4	11117.5	11073.7	11082.4
0 8 0	0 0^+ 8		11201.0	11368.5	11300.7	11234.5
2 3 0	2 0^+ 3		11756.8	11759.1	11752.5	11766.3
0 3 2	1 1^+ 3		12000.9	11998.6	12012.2	12011.6
3 1 0	3 0^+ 1	12139.2	−7.9	−2.8	−10.5	−5.4
1 6 0	1 0^+ 6		12364.0	12451.3	12350.0	12340.8
1 1 2	2 1^+ 1	12407.6	+14.7	−3.4	−4.4	−1.0
0 9 0	0 0^+ 9		12458.5	12637.1	12548.2	12504.2
2 4 0	2 0^+ 4		13185.7	13194.0	13172.0	13195.9

Note. The states are assigned, where possible, using both normal mode, (v_1, v_2, v_3), and local mode, $[m, n]^{\pm}v_2$, notations. All band origins are in cm^{-1}. For observed band origins the calculated values are given as observed − calculated; otherwise the actual calculated band origin is given.

[a] See Rothman (*30*).

[b] Band origin omitted from fits.

1. The potential energy function itself must be selected. In doing this one tries to build in known properties of the molecule: equilibrium geometry, saddle points, etc. However, if a poor function is chosen difficulty may be encountered in fitting the observed data. In the worst case a fit may be achieved at the cost of unphysical behavior in regions less sensitive to the observed data. This will of course spoil the predictive properties of the surface. In practice most studies have used the force constants of the system as a starting point for the fit.

2. The Hamiltonian used should be accurate. In practice it may be computationally convenient to approximate the kinetic energy term in the Hamiltonian. If too gross an approximation is used the surface produced will be distorted to reflect this approximation. This problem has already been encountered with a reduced dimensional Sorbie–Murrell potential energy surface for C_2H_2 (*9*, *10*).

TABLE I—*Continued*

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
0 4 2	1 1^+ 4	13498?[a]	13443.1	13433.4	13455.1	13453.7
1 7 0	1 0^+ 7		13625.5	13712.4	13610.1	13604.9
3 2 0	3 0^+ 2	13642.2[b]	+0.5	+0.7	−3.9	−5.7
0 10 0	0 0^+10		13756.6	14020.4	13849.3	13793.5
4 0 0	4 0^+ 0	13828.3	−12.3	−5.1	−1.3	−1.6
1 2 2	2 1^+ 2	13910.8	+21.5	−0.6	−0.7	−1.1
2 0 2	3 1^+ 0	14221.1	+10.6	−4.5	−9.2	−2.6
0 0 4	2 2^+ 0	14536.9	+5.0	+3.6	+4.3	−4.6
2 5 0	2 0^+ 5		14556.3	14578.1	14517.1	14549.3
0 5 2	1 1^+ 5		14760.4	14814.8	14797.3	14778.4
1 8 0	1 0^+ 8		14840.5	14904.6	14869.5	14859.1
3 3 0	3 0^+ 3	15107?[a]	15097.5	15102.4	15098.4	15109.8
0 11 0	0 0^+11		15181.1	15510.5	15228.2	15181.4
4 1 0	4 0^+ 1	15344.5	+2.6	−4.3	−2.6	−5.8
1 3 2	2 1^+ 3		15360.9	15373.3	15376.9	15377.2
2 1 2	3 1^+ 1	15742.8	+16.2	−0.9	−8.1	−1.5
2 6 0	2 0^+ 6		15842.5	15901.3	15778.1	15809.4
0 6 2	1 1^+ 6		15948.3	16105.2	16046.0	16023.8
0 1 4	2 2^+ 1		16036.2	16050.1	16060.1	16057.8
1 9 0	1 0^+ 9		16175.4	16156.6	16205.0	16187.2
3 4 0	3 0^+ 4		16511.8	16521.1	16503.3	16525.6
0 12 0	0 0^+12		16678.3	17082.1	16691.8	16654.4
1 4 2	2 1^+ 4		16760.0	16789.7	16768.2	16784.4
4 2 0	4 0^+ 2	16825.2	+6.1	−4.4	+5.7	0.0
5 0 0	5 0^+ 0	16898.4	−17.0	+5.3	−2.3	−1.3
2 7 0	2 0^+ 7		17087.3	17155.1	17030.2	17054.8
2 2 2	3 1^+ 2	17227.7	+20.1	+3.0	+1.7	+1.4
0 7 2	1 1^+ 7		17196.7	17375.7	17342.8	17312.6
3 0 2	4 1^+ 0		17452.0	17455.7	17463.4	17461.0
1 10 0	1 0^+10	17458.2	+27.2	+0.1	−11.3	+23.2
0 2 4	2 2^+ 2		17509.1	17531.4	17550.4	17542.6
1 0 4	3 2^+ 0	17748.1	+30.2	−3.1	+4.8	−6.6
3 5 0	3 0^+ 5		17877.5	17892.1	17840.7	17878.0

3. A large enough basis must be used to obtain variationally converged levels. Otherwise the energy spacings will, in general, be overestimated for a given surface and a surface which is too flat will result.

Water has long been a benchmark system for rovibrational analysis (a survey of calculations up to 1987 is given in Ref. (*11*)). The wealth of experimental data and the importance of the molecule for many applications make its potential energy surface a particularly suitable candidate for determination. Recently four empirical three-dimensional potential energy surfaces for water have been constructed (*4–7*). These surfaces all used the extensive spectroscopic data and variational calculations to demonstrate that the experimental data was reproduced. Summaries of each of these surfaces are given in Section 2.

Because of the importance of the water molecule and because we want to generate accurate spectra for the molecule over a wide frequency and temperature range, we

TABLE I—*Continued*

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
0 13 0	$0\ 0^{+}13$		18125.8	18326.2	18098.7	18119.8
1 5 2	$2\ 1^{+}\ 5$		18207.8	18158.4	18192.6	18172.1
4 3 0	$4\ 0^{+}\ 3$		18240.3	18272.5	18255.3	18257.5
2 8 0	$2\ 0^{+}\ 8$		18253.9	18538.7	18277.4	18272.2
5 1 0	$5\ 0^{+}\ 1$	18393.0	−12.7	+5.9	−14.1	−11.1
0 8 2	$1\ 1^{+}\ 8$		18561.5	18719.3	18614.7	18567.0
2 3 2	$3\ 1^{+}\ 3$		18581.5	18668.1	18656.7	18665.2
1 11 0	$1\ 0^{+}11$		18629.8	18885.2	18717.1	18684.8
3 1 2	$4\ 1^{+}\ 1$		18939.0	18953.2	18963.6	18958.6
0 3 4	$2\ 2^{+}\ 3$		18954.3	18975.7	19008.8	18996.1
			19181.0	19206.3	19099.2	19148.4
			19201.3	19248.1	19250.6	19250.9
			19330.1	19449.7	19366.8	19376.6
			19451.6	19515.4	19496.3	19493.2
			19650.8	19673.7	19646.8	19665.0
			19669.4	19698.5	19737.2	19695.6
			19786.5	19788.0	19744.6	19725.0
			19793.2	19847.0	19767.1	19757.2
			19874.3	20070.8	19884.7	19883.7
			19994.6	20372.4	20034.3	20056.2
			20021.1	20377.5	20158.3	20126.4
			20352.8	20418.1	20349.3	20377.3
			20386.8	20430.6	20400.5	20398.3
			20418.3	20451.1	20436.0	20428.5
			20523.1	20521.2	20525.7	20532.5
			20538.5	20698.6	20637.5	20638.2
			20644.6	20710.3	20711.9	20710.0
			20694.0	20775.6	20751.5	20731.8
			20829.9	20902.3	20908.5	20913.4
			20871.5	20962.5	20964.1	20914.8
			21007.3	21029.0	20995.5	21020.4
6 1 0	$6\ 0^{+}\ 1$	21221.6[b]	+6.4	−27.2	+34.8	+16.5
			21260.8	21249.4	21262.2	21276.8
			21316.3	21280.5	21289.6	21284.5
			21360.7	21427.1	21322.2	21332.5
			21366.4	21601.5	21361.5	21378.0
			21476.0	21725.9	21526.9	21545.1
			21563.1	21841.6	21716.7	21652.1
			21720.0	21871.0	21768.9	21757.7
			21793.7	21977.9	21837.3	21831.3
			21831.8	21994.6	21855.4	21842.8

have undertaken a thorough, unbiased appraisal of the four available surfaces. To do this we used a triatomic Hamiltonian which is exact within the Born–Oppenheimer approximation and large basis sets to guarantee accurate determination of the band origins. As a result we can not only assess the reliability of the four surfaces but also predict band origins for the vibrational levels for which no experimental data exist. In the next section we outline the four potential energy surfaces; in Section 3 we summarize the theory and calculations used; Section 4 presents our results and the conclusions are given in Section 5.

2. POTENTIAL ENERGY SURFACES

The four potentials, due to Carter and Handy (CH) (*4*), Halonen and Carrington (HC) (*5*), Jensen (J) (*6*), and Kauppi and Halonen (KH) (*7*), have certain features in common. They are all expressed as expansions about the equilibrium structure of water and use either *ab initio* (*12*) or empirical (*13*) force constants as a starting point. The internal coordinates used in all cases are the HÔH angle and O–H bond lengths with a Morse transformation, $y_i = 1 - \exp(-a\Delta r_i)$, for the radical coordinates. Some form of simple displacement coordinate was used for the angular functions although the exact expansion for this coordinate varied between workers. In particular CH and J chose functions which ensured that their potentials behaved correctly for linear HOH structures, while HC and KH did not.

Carter and Handy (CH) (*4*) used an exact kinetic energy operator in their Hamiltonian (*2*). They refined rather than fully optimized the empirical force constants due to Hoy, Mills, and Strey (*13*) and paid special attention to the behavior of the bending coordinate near linearity. They demonstrated that their potential satisfactorily reproduced experimental band origins and associated rotational term values with $J \leqslant 9$ for low vibrational levels and $J \leqslant 2$ for band origins up to 12 000 cm^{-1}. Unlike the other workers, CH only considered the $H_2{}^{16}O$ isotopomer.

We note that our attempts to program CH's potential directly from their published work failed as not all the data are given. An implementation of the potential was therefore obtained privately (*14*) and is available from the authors on request. Furthermore when we tried using very large radial basis sets with CH's potential a number of spurious states were encountered. Analysis of the potential function showed that these states were a result of the potential behaving unphysically for displacements of both OH bondlengths by distances of greater than $0.9a_0$ from equilibrium. In our experience such unphysical behavior at large displacements from equilibrium is a common feature of potentials which are represented as expansions about a single (equilibrium) geometry. Although in the calculations presented here we had problems only with CH's potential, it should be noted that it was only for this potential that we made our most demanding calculations—tests with up 50 Morse oscillator functions in each coordinate.

Halonen and Carrington (HC) (*5*) neglected the Watson term (*15*) in their kinetic energy operator and used a truncated expansion of the momentum dependent kinetic energy operator. Their fit was performed using only data on vibrational band origins; band origins up to 19 000 cm^{-1} were used.

Jensen (J) (*6*) used his MORBID Hamiltonian (*16*) which also involves truncation of the kinetic energy operator, although this truncation appears less drastic than that of HC and KH. J used 103 vibrational states, a similar number to HC and KH, and rotational levels with $J \leqslant 2$ where available.

Kauppi and Halonen (KH) (*7*) essentially refined the previous fit of HC by considering rotational motion. This was included using perturbation theory, unlike the calculations of CH and J who used fully coupled rovibrational basis functions to treat excited levels variationally.

All these surfaces give good representations of the water molecule over a range of nuclear displacements about equilibrium and in this region are much more accurate

TABLE II

Comparison of Observed and Calculated Band Origins for Antisymmetric Vibrational States of Water

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
0 0 1	1 0^- 0	3755.9	−0.4	+0.9	+2.8	−0.1
0 1 1	1 0^- 1	5331.2	−1.4	+0.5	−0.4	−0.9
0 2 1	1 0^- 2	6871.5	−1.2	+3.1	−0.8	−2.0
1 0 1	2 0^- 0	7249.8	+0.9	−3.7	−0.7	−1.2
0 3 1	1 0^- 3	8373.8	+0.4	+8.4	+0.1	−1.9
1 1 1	2 0^- 1	8807.0	+0.8	−3.3	−3.6	−2.7
0 4 1	1 0^- 4	9833.6	+4.1	+16.2	+1.4	+0.9
1 2 1	2 0^- 2	10328.7	+4.1	−0.4	−1.1	−3.8
2 0 1	3 0^- 0	10613.4	−3.5	−6.4	−2.9	−2.3
0 0 3	2 1^- 0	11032.4	+2.7	+1.5	+4.3	−1.8
0 5 1	1 0^- 5		11232.2	11217.3	11241.0	11235.3
1 3 1	2 0^- 3	11813.2	+9.4	+5.1	+5.0	−2.4
2 1 1	3 0^- 1	12151.3	−2.8	−5.5	−8.0	−5.4
0 1 3	2 1^- 1	12565.0	+4.9	+13.0	−8.2	−2.2
0 6 1	1 0^- 6		12565.9	12567.9	12586.7	12571.5
1 4 1	2 0^- 4	13256?[a]	13239.8	13243.4	13241.6	13252.7
2 2 1	3 0^- 2	13652.7	+4.4	−3.5	−2.9	−6.2
0 7 1	1 0^- 7		13801.5	13801.6	13831.6	13799.3
3 0 1	4 0^- 0	13830.9	−10.3	−5.6	−11.5	−1.3
0 2 3	2 1^- 2	14066.2	+8.2	−1.8	−14.5	−9.9
1 0 3	3 1^- 0	14318.8[b]	+17.4	−5.2	+5.5	−2.8
1 5 1	2 0^- 5	14640?[a]	14624.9	14628.5	14619.0	14630.4
0 8 1	1 0^- 8		14932.2	14977.5	14995.1	14932.8
2 3 1	3 0^- 3	15119.0	+13.9	+1.8	+5.8	−3.7
3 1 1	4 0^- 1	15347.9	−8.6	−4.6	−10.9	−7.5
0 3 3	2 1^- 3		15521.8	15529.1	15551.6	15545.4
1 1 3	3 1^- 1	15832.8	+22.4	−8.2	−6.7	−6.5
1 6 1	2 0^- 6		15943.7	15952.5	15919.3	15922.9
0 9 1	1 0^- 9		16074.8	16187.4	16167.3	16108.3
2 4 1	3 0^- 4		16521.5	16536.0	16524.3	16541.3
3 2 1	4 0^- 2	16821.6	+3.5	−10.4	+6.4	−2.4

Note. See Table I for further explanation.

[a] See Rothman (*30*).

[b] Band origin omitted from fits.

than the best *ab initio* surfaces presently available or achievable for water. The comparative terms used below are thus a reflection of the relative rather than absolute merits of these four surfaces.

3. METHOD

Calculations were performed using Radau coordinates (*17, 18*). For systems such as water with a heavy central atom, Radau coordinates are very similar to the bond length–bond angle coordinates in which the potential energy surfaces are expressed. They have the advantage, important for work within a Discrete Variable Representation (*19*), that they are orthogonal, i.e., that they give a diagonal kinetic energy operator. Transformation of the potential between different coordinate systems can of course be achieved without loss of accuracy.

TABLE II—*Continued*

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
4 0 1	5 0^- 0	16898.8	−16.3	+5.2	−1.6	−0.9
0 4 3	2 1^- 4		16948.2	16947.2	16982.8	16974.8
1 7 1	2 0^- 7		17187.0	17198.4	17162.0	17156.9
1 2 3	3 1^- 2	17312.5	−11.6	−9.5	−8.2	−8.0
0 10 1	1 0^-10		17280.8	17513.8	17436.2	17375.0
2 0 3	4 1^- 0	17495.5	+20.5	−2.3	+6.2	−1.7
2 5 1	3 0^- 5		17891.7	17907.0	17879.5	17903.3
0 0 5	3 2^- 0		17940.3	17936.5	17940.9	17955.1
3 3 1	4 0^- 3	18265.8^b	+13.8	−7.2	+16.8	+4.7
0 5 3	2 1^- 5		18321.2	18313.8	18324.6	18310.3
1 8 1	2 0^- 8		18336.4	18363.4	18388.7	18371.0
4 1 1	5 0^- 1	18393.3	−12.2	+5.6	−15.4	−11.7
0 11 1	1 0^-11		18671.5	18948.8	18776.8	18713.4
1 3 3	3 1^- 3		18716.9	18765.2	18762.7	18764.4
2 1 3	4 1^- 1	18990.0	+28.8	−3.9	−7.6	−6.6
2 6 1	3 0^- 6		19204.8	19220.9	19161.5	19189.0
0 1 5	3 2^- 1		19415.6	19432.6	19450.6	19449.5
1 9 1	2 0^- 9		19422.9	19515.7	19493.7	19468.7
0 6 3	2 1^- 6		19647.8	19629.6	19651.0	19667.4
3 4 1	4 0^- 4		19665.2	19677.4	19718.4	19698.1
5 0 1	6 0^- 0	19781.1^b	−5.3	−7.0	+41.0	+23.6
4 2 1	5 0^- 2		19874.3	19847.7	19886.8	19884.5
0 12 1	1 0^-12		20090.6	20453.3	20187.8	20126.3
1 4 3	3 1^- 4		20116.1	20167.1	20161.7	20165.8
2 7 1	3 0^- 7		20399.7	20472.4	20398.6	20416.3
2 2 3	4 1^- 2		20448.4	20456.1	20443.8	20449.8
3 0 3	5 1^- 0	20543.1^b	+19.3	+11.9	+7.3	+0.7
1 10 1	2 0^-10		20605.5	20779.5	20758.5	20723.0
0 2 5	3 2^- 2		20928.3	20894.2	20917.8	20910.9
0 7 3	2 1^- 7		20859.5	20864.9	20977.7	20948.3
1 0 5	4 2^- 0		21001.3	21031.8	21027.2	21026.0
3 5 1	4 0^- 5		21006.7	21035.4	21003.4	21052.2
5 1 1	6 0^- 1	21221.8^b	+6.6	−28.0	+32.2	15.8
4 3 1	5 0^- 3		21316.5	21281.4	21337.6	21338.6
0 13 1	1 0^-13		21473.5	21520.3	21489.2	21499.0
1 5 3	3 1^- 5		21547.9	21612.1	21575.9	21566.5
2 8 1	3 0^- 8		21598.1	21998.6	21683.3	21623.0
2 3 3	4 1^- 3		21808.0	21879.3	21860.3	21866.7

Two different programs were used for calculating the vibrational band origins; both used exact kinetic energy operators (*18*). Initially calculations were performed using the TRIATOM program suite (*20*) which uses basis set expansions and is thus strictly variational. Final results for band origins ($J = 0$ states) were obtained using a program which employed a Discrete Variable Representation (DVR) in the angular coordinate (*21–23*). In both cases functions based on Morse oscillators (*1*) were used for the radial coordinates. Variationally optimized parameters (*20*) for these were found to be $r_e = 2.06\ a_0$, $\omega_e = 0.014\ E_h$, and $D_e = 0.14\ E_h$.

Initial convergence tests were performed for the symmetric (A_1) band origins using TRIATOM and CH's surface. These showed that vibrational levels up to 22 000 cm^{-1} above the ground state were well converged by basis sets containing 30 or more Legendre polynomials in the angular basis set expansion. Conversely basis sets with up

TABLE III

Comparison of Observed and Calculated Term Values with $J = 1$ for the Lowest 10 Vibrational States of Water

(v_1,v_2,v_3)	(K_a,K_c)	Expt	CH	HC	KH	J
0 0 0	0 1	23.79	−0.05	−0.13	−0.04	−0.01
	1 1	37.14	+0.04	−0.03	−0.03	+0.06
	1 0	42.36	+0.00	−0.10	−0.06	+0.03
0 1 0	0 1	23.81	−0.06	−0.02	−0.07	−0.01
	1 1	40.22	+0.07	−0.33	+0.00	+0.04
	1 0	45.76	+0.03	−0.30	−0.03	+0.04
0 2 0	0 1	23.81	−0.07	+0.08	−0.11	−0.01
	1 1	44.46	+0.08	−0.76	+0.10	+0.07
	1 0	50.28	+0.04	−0.66	+0.04	+0.06
1 0 0	0 1	23.40	−0.05	−0.38	−0.05	−0.03
	1 1	36.24	+0.14	+0.30	+0.00	+0.00
	1 0	41.43	+0.08	+0.07	−0.04	−0.02
0 0 1	0 1	23.56	−0.09	−0.22	−0.04	−0.04
	1 1	35.77	+0.07	−0.10	−0.14	−0.03
	1 0	41.06	+0.02	−0.18	−0.12	−0.03
0 3 0	0 1	23.77	−0.09	+0.15	−0.18	−0.05
	1 1	50.66	+0.05	−1.40	+0.38	+0.13
	1 0	56.74	+0.02	−1.22	+0.28	+0.11
1 1 0	0 1	23.42	−0.09	−0.27	−0.07	−0.02
	1 1	39.17	+0.24	+0.10	−0.07	−0.04
	1 0	44.68	+0.16	−0.03	−0.11	−0.05
0 1 1	0 1	23.63	−0.08	−0.07	−0.02	+0.00
	1 1	38.52	+0.17	−0.43	−0.15	−0.05
	1 0	44.13	+0.10	−0.41	−0.14	−0.04
0 4 0	0 1	23.73	−0.08	+0.25	−0.24	−0.06
	1 1		60.75	62.98	59.58	60.43
	1 0	67.04	−0.03	−2.00	1.02	+0.29
1 2 0	0 1		23.53	23.59	23.52	23.44
	1 1		42.82	43.35	43.33	43.27
	1 0		48.72	49.22	49.18	49.08

Note. The states are assigned using normal mode, (v_1, v_2, v_3), and rigid rotor, notation. All term values are in cm^{-1}. For observed levels the calculated values are given as observed − calculated; otherwise the actual calculated term value is given.

12 Morse oscillator-like functions in the (symmetrized (*23*)) radial basis only satisfactorily converged states lying below the (5, 0, 0) stretching overtone (observed band origin 16 898.4 cm^{-1}).

The prediagonalizations involved in the DVR calculations allow much larger radial basis sets to be used at very little extra computational expense (*19, 22*). Calculations were therefore performed with 22 Morse oscillator-like functions, 40 angular grid points (the equivalent of 40 Legendre polynomials), and a final, energy selected Hamiltonian of dimension $N = 1250$. Tests with 20 and 25 Morse functions, 48 angular grid points, and $N = 1000$ suggested that this calculation converged all the band origins below 22 000 cm^{-1} to 0.1 cm^{-1} or better.

The DVR calculations are similar to those performed by Bačić *et al.* (*24*) on water. Bačić *et al.* employed smaller basis sets as they only aimed for convergence of about 1–2 cm^{-1} for their higher levels. They used a realistic, rather than fully quantitative,

TABLE IV

Comparison of Observed and Calculated Term Values with $J = 2$ for the Lowest 10 Vibrational States of Water

(v_1,v_2,v_3)	(K_a,K_c)	Expt	CH	HC	KH	J
0 0 0	0 2	70.09	−0.11	−0.35	−0.11	−0.02
	1 2	79.50	−0.02	−0.23	−0.09	+0.05
	1 1	95.18	−0.09	−0.39	−0.13	+0.01
	2 1	134.90	+0.13	−0.12	−0.10	+0.20
	2 0	136.20	+0.15	−0.11	−0.07	+0.22
0 1 0	0 2	70.22	−0.16	−0.10	−0.18	−0.01
	1 2	82.32	−0.02	−0.40	−0.10	+0.05
	1 1	98.90	−0.13	−0.32	−0.20	+0.02
	2 1	147.56	+0.25	−1.23	+0.01	+0.17
	2 0	148.74	+0.22	−1.21	−0.01	+0.17
0 2 0	0 2	70.33	−0.18	+0.16	−0.30	−0.03
	1 2	86.29	−0.01	−0.71	−0.05	+0.06
	1 1	103.71	−0.13	−0.41	−0.23	+0.02
	2 1	164.51	+0.32	−2.84	+0.42	+0.26
	2 0	165.58	+0.30	−2.77	+0.39	+0.26
1 0 0	0 2	68.89	−0.11	−0.97	−0.14	−0.08
	1 2	77.84	+0.08	−0.24	−0.08	−0.05
	1 1	93.41	−0.05	−0.89	−0.17	−0.09
	2 1	131.64	+0.51	+1.11	−0.01	+0.01
	2 0	132.92	+0.48	+0.96	−0.03	+0.00
0 0 1	0 2	69.29	−0.22	−0.60	−0.11	−0.10
	1 2	77.66	−0.04	−0.43	−0.20	−0.07
	1 1	93.45	−0.21	−0.71	−0.18	−0.13
	2 1	129.81	+0.26	−0.34	−0.47	−0.08
	2 0	131.18	+0.21	−0.40	−0.47	−0.09
0 3 0	0 2	70.40	−0.21	+0.40	−0.46	−0.08
	1 2	92.21	−0.04	−1.23	+0.15	+0.09
	1 1	110.39	−0.16	−0.72	−0.15	+0.03
	2 1	188.49	+0.30	−5.13	+1.47	+0.54
	2 0	189.41	+0.28	−5.03	+1.42	+0.54
1 1 0	0 2	69.02	−0.21	−0.72	−0.20	−0.07
	1 2	80.51	+0.14	−0.29	−0.18	−0.07
	1 1	97.03	−0.07	−0.68	−0.27	−0.09
	2 1	143.76	+0.92	+0.45	−0.22	−0.10
	2 0	144.97	+0.88	+0.38	−0.23	−0.10
0 1 1	0 2	69.49	−0.26	−0.31	−0.13	−0.06
	1 2	80.17	+0.02	−0.63	−0.23	−0.09
	1 1	96.93	−0.19	−0.60	−0.23	−0.10
	2 1	141.11	+0.55	−1.63	−0.60	−0.25
	2 0	142.42	+0.51	−1.60	−0.58	−0.24
0 4 0	0 2	70.43	−0.20	+0.67	−0.64	−0.15
	1 2	102.03	−0.09	−1.95	+0.87	+0.26
	1 1		121.04	122.10	120.43	120.69
	2 1		224.87	233.16	220.96	223.80
	2 0		225.61	233.80	221.75	224.55
1 2 0	0 2		69.38	69.62	69.43	69.19
	1 2		84.00	84.69	84.55	84.37
	1 1		101.64	102.25	102.07	101.76
	2 1	159.92	+1.49	−0.49	−0.38	−0.19
	2 0	161.01	+1.44	−0.49	−0.39	−0.19

Note. See Table III for further explanation.

potential energy surface due to Sorbie and Murrell (*25*), used previously for extensive variational calculations by Johnson and Reinhardt (*26*).

The calculations for $J = 1$ and $J = 2$ were performed using basis functions and a two-step variational procedure as implemented in programs SELECT, TRIATOM, and ROTLEVD (*20*). As we are only interested in results for the lowest 10 vibrational states, only modest variational basis sets were employed. Vibrational basis functions were selected from nine candidate Morse-like functions in each radial coordinate and 24 (associated) Legendre polynomials in the angular coordinates. For technical reasons the body-fixed z-axis was placed along one of the Radau stretching coordinates which means that both symmetric and antisymmetric vibrations were treated in the same calculation (*27*). In the first step, which assumes that k, the projection of J along the body-fixed z-axis, is a good quantum number, 800 basis functions were retained in the calculation. In the second step, the lowest 300 solutions of the first step were then selected by energy to diagnoalize the full Hamiltonian. This procedure converged all the term values (energy differences $J_{K_a,K_c} - 0_{00}$ for each variational state) to 0.01 cm^{-1} or better.

TABLE V

Statistical Comparison of the four Potentials for the 62 Observed Band Origins and the Rotational Term Values

Potential	Band origins		Term values	
	mean	σ	mean	σ
CH	4.1	11.5	0.10	0.35
HC	-1.2	7.2	-0.59	1.20
KH	0.2	10.3	-0.05	0.37
J	-1.1	6.4	0.01	0.14

Note. Given are the mean (observed − calculated) error and standard deviation (σ), both in cm^{-1}.

4. RESULTS AND DISCUSSION

Tables I and II present our band origins for the four potential energy surfaces considered for symmetric and antisymmetric states, respectively. Where the band origin is known experimentally our results are presented as a difference from this value. For the other states, the predicted value of the band origin is given. All calculations are for $H_2{}^{16}O$.

In Tables I and II the band origins have been assigned using both normal mode, (v_1, v_2, v_3), and local mode, $[m, n]^{\pm}v_2$, notation. In doing this we have followed HC and KH, rather than for example J whose method of assigning some of the higher stretching states is different. Assignments of observed levels were made by simple energy comparisions; in the few cases where this led to any ambiguity we were guided by the previous results for a given potential.

For the unobserved levels, assignments were made by using energy differences for series of levels. Clearly this method only yields a unique solution for those band origins where the spacing between adjacent levels with the same symmetry is reasonably large. For higher energies our assignments become increasingly less secure and for symmetric band origins above 19 000 cm^{-1} we could not give any assignments since the procedure has broken down by this point. Bačić *et al.* (*24*) did not attempt assignments to band origins above 15 300 cm^{-1} (symmetric) and 17 400 cm^{-1} (antisymmetric). Instead these authors noted that, at least for their potential, the higher levels showed behavior often associated with quantum chaos. Again this may be taken as evidence that our higher assignments should be viewed with caution.

Close examination of Tables I and II shows that the surfaces do not all give the band origins in the same order. The effect is most noticeable for the high lying bending states, particularly with the HC potential. Where the effect is reasonably clear cut we have allowed for it by tabulating the band origins out of energy sequence. However, for band origins which are closely spaced in energy, it is difficult to make such corrections with any confidence and we have therefore not attempted them.

Most of the experimental band origins quoted in Tables I and II are taken from J (*6*) who gives a comprehensive set of references. However, some of the band origins measured by Camy-Peyret *et al.* (*28*) and Mandin *et al.* (*29*) appear not to have been considered in any of the previous works (*4–7*). These band origins are indicated in the tables. Furthermore HC and KH tabulated the local mode pair $[4, 0]^{\pm}2$ the wrong way round. Finally, Rothman (*30*) gives a number of band origins labelled, without explanation, as '?'. We have included these in the tables for comparison but not used them in assessing the potentials. We note, however, that most of these band origins lie close to the predictions from J's potential for the same state.

Tables III and IV give our term values for $J = 1$ and $J = 2$, respectively. It is noteworthy that while for HC, KH, and J's potentials the poorest results are for the (0, 3, 0) bending overtone, CH's potential reproduces these levels satisfactorily but performs poorly for the (1, 1, 0) combination band.

Table V summarizes our statistical analysis of variational and rotational comparisons contained in Tables I–IV. We have kept the analyses separate as the errors in reproducing the band origins are so much larger that they would obscure the information about the behavior of the potentials under rotational excitation.

Considering the four potentials in turn: our results for CH's potential are generally in good agreement with, but not identical to, those quoted by CH. This potential overestimates the observed band origins by an average of 4.1 cm^{-1}, with a standard deviation of 11.5 cm^{-1}. This relatively poor performance compared to the potentials discussed below is undoubtedly due to the fact that this potential was not fully refined by an iterative procedure. We note however that the potential performs fairly consistently over the energy range considered and, probably because of the care taken as the molecule becomes linear, gives good results for the rotationally excited states.

Our band origins for HC's potential are generally slightly higher than those obtained by HC. As our results are very well converged, this problem cannot be variational in nature and we suspect it is a result of HC's approximation of their kinetic energy operator. We find that HC's potential overestimates the band origins by an average of 1.2 cm^{-1}, with a standard deviation of 7.2 cm^{-1}. This is of course worse than the standard deviation of 4 cm^{-1} quoted by HC but the difference is largely explained by the inclusion of more high lying band origins in our comparison. Although the HC potential reproduces the observed band origins with excitation in the bending mode, its predictions for the as yet unobserved states with more than 5 quanta of excitation in the bending mode appear erratic. This is particularly true of the (0, 12, 0) and (0, 13, 0) band origins which are hundreds of wavenumbers above the predictions of the other 3 potentials. Similarly this potential gives notably poor results for the rotationally excited states.

The agreement between the observed − calculated residuals obtained for the band origins by J and us is in line with comparisons made by J using his MORBID Hamiltonian and an exact kinetic energy operator for CH_2 (*16*). We find that J's potential on average overestimates the band origins by 1.1 cm^{-1}, with a standard deviation of 6.4 cm^{-1}. These results may appear poor when compared to the standard deviation of 0.63 cm^{-1} with which J reproduced his input data. However, it should be remembered that J weighted high band origins by 0.1 and fitted a large number of rotational term values. We find that his potential reproduces our more limited rotational data set with almost no mean error and a standard deviation of only 0.14 cm^{-1}. A notable feature of J's potential is that between 8 500 and 17 000 cm^{-1} for the symmetric states and 10 000 and 18 000 cm^{-1} for antisymmetric states all the band origins are overestimated. This suggests that his potential contains a small systematic error, perhaps introduced by his MORBID hamiltonian. For unobserved states which have any significant bending excitation, J's potential generally gives band origins in reasonable agreement with CH's. As both these potentials have been constrained to give the correct behavior for quasilinear geometries and give good results for rotational excitation, these band origins should be fairly reliable.

Although KH's potential is the most recent it does not perform particularly well for the band origins, with a standard deviation of 10.3 cm^{-1}. This is notably worse than the similar HC potential which actually had fewer parameters. However, we note that KH's potential is considerably better than HC's for the rotational term values.

5. CONCLUSIONS

We have tested potential energy surfaces for the water molecule by comparison with 62 observed band origins below 22 000 cm^{-1} and 74 observed term values. The four spectroscopically determined potentials tested reproduce the observed band origins to about 0.1% and rotational term values to 1% or better. Of these four potentials, the one due to Jensen (*6*) is undoubtedly the most accurate. Although it is possible that Jensen's potential could be further improved by correcting a small systematic error in the band origins in the 10 000 to 17 000 cm^{-1} range, the potential appears to be reliable over the whole energy regime considered. We therefore regard our estimates for the unobserved band origins up to 22 000 cm^{-1} obtained using Jensen's potential as the most reliable available.

It is our plan to use this potential as the basis for further studies of the water molecule. In particular we wish to calculate the effect of water in atmospheric and astronomical situations, including the atmospheres of cool stars. As we would like to obtain spectra including intensities, not just transition frequencies, it will be necessary for us to consider the dipole function of the molecule. Surprisingly, given the fundamental nature and general importance of water not to mention the wealth of absolute intensity measurements, there appears at present to be no reliable dipole surface available for this system.

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