

# Spectroscopically determined potential energy surface of $\text{H}_2^{16}\text{O}$ up to $25\,000\text{ cm}^{-1}$

Sergei V. Shirin, Oleg L. Polyansky, Nikolai F. Zobov,  
*Institute of Applied Physics, Russian Academy of Science,*  
*Uljanov Street 46, Nizhnii Novgorod, Russia 603950,*  
*and Department of Physics and Astronomy,*  
*University College London, London WC1E 6BT, UK*

Paolo Barletta and Jonathan Tennyson\*  
*Department of Physics and Astronomy,*  
*University College London, London WC1E 6BT, UK*

(Dated: September 26, 2002)

## Abstract

A potential energy surface for the major isotopomer of water is constructed by fitting to observed vibration-rotation energy levels of the system using the exact kinetic energy operator nuclear motion program DVR3D. The starting point for the fit is the *ab initio* Born Oppenheimer surface of Partridge and Schwenke (J. Chem. Phys., **106**, 4618 (1997)) and corrections to it: both one- and two-electron relativistic effects, a correction to the height of the barrier to linearity, allowance for the Lamb shift and the inclusion of both adiabatic and non-adiabatic non-Born-Oppenheimer corrections. Fits are made by scaling the starting potential by a morphing function, the parameters of which are optimised. Two fitted potentials are presented which only differ significantly in their treatment of rotational non-adiabatic effects. Energy levels up to  $25468\text{ cm}^{-1}$  with  $J = 0, 2$  and  $5$  are fitted with only 20 parameters. The resulting potentials predict experimentally known levels with  $J \leq 10$  with a standard deviation of  $0.1\text{ cm}^{-1}$ , and are only slightly worse for  $J = 20$ , for which rotational non-adiabatic effects are significant. The fits showed that around 100 ‘known’ energy levels are probably the result of mis-assignments. Analysis of mis-assigned levels above  $20\,000\text{ cm}^{-1}$  leads to the reassignment of 23 transitions.

---

\*Electronic address: [j.tennyson@ucl.ac.uk](mailto:j.tennyson@ucl.ac.uk)

## I. INTRODUCTION

Variational calculations can predict vibration-rotation energy levels of triatomic molecules to an accuracy which is normally governed by the accuracy of the underlying potential energy surface. As a result, variational calculations are now regularly being used to determine potential energy surface of triatomics; examples for which high accuracy potentials have been determined by this method include  $\text{H}_3^+$  [1, 2],  $\text{H}_2\text{Te}$  [3],  $\text{O}_3$  [4],  $\text{CO}_2$  [5],  $\text{H}_2\text{S}$  [6] and  $\text{HO}_2$  [7]. These surfaces are, at least in principle, sufficient to determine all the vibrational and rotational energy levels and wavefunctions in the energy range for which they are valid. Given a suitable *ab initio* starting potential, they can usually be determined by fitting a relatively small number of parameters; often significantly less than would be use to characterize a single vibrational state using more traditional effective Hamiltonian approaches.

The spectrum of water and hence its ground state potential energy surface are of particular importance for a large variety of applications. This and the fact that water is particularly poorly treated using perturbation theory [8] has led to the construction of several spectroscopically determined potential surfaces [9–18]. The most important of these surfaces are summarized in Table I. Table I shows a steady improvement of the fitted potentials with time. As will be discussed below, this improvement correlates strongly with the use of improved *ab initio* electronic potentials as the starting point. Partridge and Schwenke (henceforth PS) [18] computed a particularly good *ab initio* potential for water which, to a large extent, accounts for the excellence of their fit, data from which has been widely used. Detailed comparisons are made below with results obtained using PS’s fitted potential and these demonstrate its high quality.

Not included in Table I are the results of Xie and Yan [17]. These workers fitted 70 vibrational band origins of  $\text{H}_2^{16}\text{O}$  with an accuracy of  $1.17\text{ cm}^{-1}$ . However their potential proved to give very poor results when rotational excitation is included [19]. This illustrates an important point: when fitting spectroscopically determined potentials for light systems such as water, it is important to treat both vibrational and rotational motion.

The concept of a potential is, of course, based on the separation of electronic and nuclear motion. The breakdown of this, Born-Oppenheimer or adiabatic, approximation has already been explicitly allowed for in spectroscopically determined potentials of  $\text{H}_3^+$  and its isotopomers [1]. Tests using *ab initio* surfaces suggest that for water, breakdown of the

TABLE I: Summary of spectroscopically determined H<sub>2</sub><sup>16</sup>O potential energy surfaces.

Reference	Year	$\sigma_{\text{vib}}^a$	$N_{\text{vib}}^b$	$E_{\text{max}}^c$
Hoy, Mills & Strey [16]	1972	214.	25	13 000
Carter & Handy [9]	1987	2.42	25	13 000
Halonen & Carrington [10]	1988	5.35	54	18 000
Jensen [11]	1989	3.22	55	18 000
Polyansky <i>et al.</i> (PJT1) [14]	1994	0.60	40	18 000
Polyansky <i>et al.</i> (PJT2) [13]	1996	0.94	63	25 000
Partridge & Schwenke [18]	1997	0.33	42	18 000
This work	2002	0.10	105	25 000

<sup>a</sup> $\sigma_{\text{vib}}$  is the standard deviation of the fitted vibrational levels in cm<sup>-1</sup>.

<sup>b</sup> $N_{\text{vib}}$  is the number of vibrational levels used in the fit.

<sup>c</sup> $E_{\text{max}}$  is the maximum energy of the fitted vibrational levels in cm<sup>-1</sup>.

Born-Oppenheimer approximation becomes important if sub 1 cm<sup>-1</sup> accuracy is desired [20–22].

In this work we use the increased data set of experimentally determined H<sub>2</sub><sup>16</sup>O energy levels of Tennyson *et al.* [23] to fit a ground state potential energy surface which is valid over the entire range of known rotation-vibration energy levels for the system. To do this we use not only the high quality *ab initio* potential of PS as a starting point, but augment this potential with *ab initio* estimates of relativistic [24, 25], adiabatic [22] and even quantum electronic dynamic [26] corrections to the potential. Furthermore, allowance is explicitly made for both vibrational and rotational non-adiabatic effects although, of course, such terms do not form part of a potential. The result is surfaces of unrivalled accuracy for the ground electronic state of H<sub>2</sub><sup>16</sup>O.

## II. METHOD

All potentials below are functions of the standard bondlength, bondangle coordinates of water,  $(r_1, r_2, \theta)$ . Their equilibrium values  $r_e$  and  $\theta_e$  were taken as 1.80965034  $a_0$  and 1.82404493 radians respectively. All nuclear motion calculations were performed using Radau coordinates with the ‘bisector’ axis embedding which places the  $x$ -axis so that it

bisects the bond angle and the  $z$ -axis in the molecular plane [27, 28].

Experience has shown that the quality of a spectroscopically determined potential depends strongly on the quality of the starting point which is usually, as here, taken from *ab initio* calculations. Our starting point was the Born-Oppenheimer  $V^{5z} + \Delta V^{\text{core}}$  potential due to Partridge and Schwenke (PS) [18] which is the best published *ab initio* potential. This potential was then augmented, as detailed below, by corrections to allow relativistic effects. As discussed by Kain *et al.* [29], when augmented by these corrections, the PS potential gives good results for the stretching coordinates but is significantly too steep in the bending coordinate. Kain *et al.* developed a one-dimensional correction to the bending motion,  $\Delta V_B(\theta)$ , given by:

$$\Delta V_B(\theta) = F \frac{(\theta^3 - \theta_e^3)}{(\theta_e^3 - \pi^3)} + G \frac{(\theta^5 - \theta_e^5)}{(\theta_e^5 - \pi^5)} + (\Delta B + F + G) \frac{(\theta^2 - \theta_e^2)}{(\theta_e^2 - \pi^2)} \quad (1)$$

where the parameters  $F = 879.7 \text{ cm}^{-1}$ ,  $G = -381.1 \text{ cm}^{-1}$  and  $\Delta B = -87.5 \text{ cm}^{-1}$  were determined to give the correct shape and magnitude to the correction term. In particular the parameter  $\Delta B$  gives the change in the height of the barrier to linearity.

The general form for the fitted potential used by us is

$$V_{\text{fit}}(r_1, r_2, \theta) = f_{\text{morp}}(r_1, r_2, \theta) V_{ai}(r_1, r_2, \theta) + \Delta V_B(\theta) \quad (2)$$

where  $V_{ai}$  is the *ab initio* starting point,  $f_{\text{morp}}$  is a morphing function [30, 31], the parameters of which we fit, and  $\Delta V_B(\theta)$  is the barrier correction discussed above. The morphing function is expressed as a power series in so-called Jensen coordinates [11]:

$$\begin{aligned} s_1 &= \frac{r_1 + r_2}{2} - r_e \\ s_2 &= \cos \theta - \cos \theta_e \\ s_3 &= \frac{r_1 - r_2}{2} \end{aligned} \quad (3)$$

$$f_{\text{morp}} = c_{000} + \sum_{ijk} c_{i,j,k} s_1^i s_2^j s_3^k \quad 2 \leq i + j + k \leq N \quad (4)$$

where the value of  $N$  is known as the order of the fit and the parameters  $c_{i,j,k}$  are determined by least-squares fitting to the experimental data. The purpose of the morphing function is to provide a smooth means of adjusting the starting potential.

It should be noted that PS's fit to their *ab initio* data is designed so that the surface allows dissociation to the correct energy. Our fitting procedure relaxes this constraint, something

we have in any case found necessary in fitting new, higher accuracy *ab initio* data [32]. As is usual with fitted potentials, the range of validity may not extend far beyond the range of the data used to fit it. However there is a well-established procedure for incorporating spectroscopically determined potentials into global surfaces [33].

An important aspect of the present work is consideration of corrections which go beyond the Born-Oppenheimer approximation. These take three forms. The simplest to include is the adiabatic correction, also known as the Born-Oppenheimer Diagonal Correction (BODC), which takes the form of an extra, isotopomer-dependent potential term,  $\Delta V_{\text{ad}}$ . In this work we use the  $\text{H}_2^{16}\text{O}$  adiabatic correction due to Schwenke [22] as refitted by us to extend its range of validity [20].

Below, we present two separate fits to the spectroscopic data, denoted A and B. These fits differ essentially in the treatment of the non-adiabatic effects. In both fits the vibrational mass was determined using nuclear masses for the particles. In fit A the effective rotational mass was taken as the mid-point between that given by using nuclear and atomic masses, see Zobov *et al.* [21] while in fit B nuclear masses were also used for the rotational motion.

Accurate studies on diatomics have for some time used effective masses to model vibrational non-adiabatic effects [34, 35]. For water such a formulation was originally presented by Bunker and Moss [36]. Here vibrational non-adiabatic effects were included using the two-term correction of Tennyson *et al.* [20] which was found to be a good approximation to the full vibrational non-adiabatic treatment of Schwenke [22]. This corrections to the Born-Oppenheimer nuclear motion Hamiltonian [28] can be implemented as a change to the effective mass for standard vibrational kinetic energy operators:

$$\frac{1}{\mu} \frac{\partial^2}{\partial r_i^2} \rightarrow \left( \frac{1}{\mu} + A \right) \frac{\partial^2}{\partial r_i^2} \quad i = 1, 2 \quad (5)$$

and an extra angular kinetic energy operator:

$$B \frac{\partial^2}{\partial \theta^2} \quad (6)$$

where the values  $A = -1.0602 \times 1.0275213 \times 10^{-7}$  and  $B = -1.4062589 \times 10^{-8}$  a.u. were taken from Schwenke [22]; note that the factor of 1.0602 in  $A$  results from a difference in the definition of Radau coordinates. Schwenke employs coordinates such that  $\mu = m_H$  whereas with our definition the reduced mass also depends on the oxygen mass [28].

As discussed by Polyansky and Tennyson [37], using different effective masses between the angular vibrational and rotational kinetic energy operators introduces an extra term

into the Hamiltonian. In this case its matrix element can be written as:

$$B\delta_{k',k} \langle j', k' | \frac{k^2}{\sin^2 \theta} | j, k \rangle, \quad (7)$$

where  $|j, k \rangle$  is an associated Legendre function in  $\cos \theta$ .

A similarly simplified treatment, suggested by Schwenke [22], of his full rotational non-adiabatic calculation is given by adding the following extra term to the standard, Radau bisector, nuclear motion kinetic energy operator [27, 28]:

$$\begin{aligned} \hat{K}_{VR}^{\text{non-ad}} = & \delta_{k',k} J(J+1) \langle j', k' | \frac{\epsilon_{xx} + \epsilon_{yy}}{2} | j, k \rangle \\ & + k^2 \langle j', k' | \epsilon_{zz} - \frac{\epsilon_{xx} + \epsilon_{yy}}{2} | j, k \rangle + \delta_{k',k \pm 2} C_{J,k \pm 1}^{\pm} C_{J,k}^{\pm} \langle j', k' | \frac{\epsilon_{xx} - \epsilon_{yy}}{4} | j, k \rangle \end{aligned} \quad (8)$$

where

$$C_{J,k}^{\pm} = [J(J+1) - k(k \pm 1)]^{\frac{1}{2}}, \quad (9)$$

and the constants  $\epsilon_{ii}$ , values for which were taken from Schwenke [22], give the magnitude of the rotational non-adiabatic effect.

Extensive tests showed that we were unable to obtain a good fit to energy level data without explicit inclusion of the allowance for non-adiabatic effects which went beyond simple manipulation of effective masses. A number of methods of allowing for non-adiabatic effects were tested, most of which worsened rather than improved our fit. However two methods of including rotational non-adiabatic effects yielded satisfactory fits to the data; details of these fits are given below.

Fit A included most of the non-adiabatic corrections described above but omitted both the extra term (7) and the off-diagonal in  $k$  term in the rotational non-adiabatic operator (8). To our surprise, fits using this model led to a systematic error for higher rotationally excited states which depended on the degree of rotational excitation as  $J(J+1)$  but was independent of vibrational state and the rotational quantum numbers  $K_a$  and  $K_c$ . Such an effect cannot arise solely from the potential. We therefore attributed it to neglected non-adiabatic effects and added a term  $RJ(J+1)$  to the kinetic energy operator.  $R = \frac{1}{600} \text{ cm}^{-1}$  was found to be the optimal value for this extra term. The potential resulting from this fit is labelled PES A below.

Fit B included all non-adiabatic corrections detailed above but used  $\epsilon_{ii}$  as adjustable parameters. The best fit was obtained by using  $0.8\epsilon_{xx}$ ,  $0.8\epsilon_{yy}$  and  $-1.1\epsilon_{zz}$ , where  $\epsilon_{ii}$  are the

values given in Table 4 of Schwenke [22]. The potential resulting from this fit is labelled PES B below.

For fit A, the *ab initio* starting point was given by

$$V_{ai} = V^{5z} + \Delta V^{\text{core}} + \Delta V_1^{\text{rel}} + \Delta V_2^{\text{rel}} + \Delta V_{\text{ad}}, \quad (10)$$

where  $\Delta V_1^{\text{rel}}$  and  $\Delta V_2^{\text{rel}}$  are the first-order [24] and second-order [25] electronic relativistic corrections, and the other terms have been defined earlier. For fit B,  $V_{ai}$  was augmented with one-electron Lamb shift surface of Pyykko *et al.* [26].

### III. RESULTS

All nuclear motion calculations were performed with the DVR3D program suite [38] in Radau coordinates and a body-fixed axis embedding which places the  $x$ -axis along the bisector of the angle [28]. A new module, XPECT3, for calculating expectation values of geometric operators has been added to these programs. XPECT3 was used to obtain derivatives of the morphing constants using the Hellman-Feynmann theorem. A new version of the DVR3D program suite which includes XPECT3 is currently being prepared for publication [39].

Vibrational calculations were performed with 29 radial grid points, based on Morse oscillator-like functions, 40 Gauss (associated) Legendre angular grid points and a final Hamiltonian of dimension 1500. For the rotationally excited states, the lowest 500 ‘vibrational’ functions were retained for each value of  $k$  ( $\approx K_a$ ) and final Hamiltonians of dimension 1500 and 2400 were diagonalized for  $J = 2$  and 5 respectively. Detailed discussion of these parameters can be found in ref [38].

It is both computationally expensive and unnecessary to perform fits for all rotational energy levels simultaneously. We therefore performed systematic fits using all levels given by Tennyson *et al.* [23] with  $J = 0, 2$  and 5. In addition, calculations were periodically performed for  $J = 10, 20$  and 30 to gauge the high- $J$  behavior of any model. These high  $J$  levels proved particularly sensitive to the rotational non-adiabatic treatment.

During the fit it became apparent that a number of the experimentally determined energy levels were incorrect. This is to be expected since the assignment of water spectra is difficult and previous improvements in theoretical techniques have similarly led to reassignments

TABLE II: Reassigned high-frequency transitions of  $\text{H}_2^{16}\text{O}$ , data from [42–44]. All transitions are from the (000) vibrational state.

$\omega/\text{cm}^{-1}$	$J'$	$K'_a$	$K'_c$	$J''$	$K''_a$	$K''_c$	$v'_1 v'_2 v'_3$
25184.93728	6	1	5	5	1	4	701
24000.63215	3	2	2	2	2	1	611
22626.27772	3	2	1	2	1	2	700
22606.56910	6	2	4	5	2	3	601
22605.60314	3	2	2	2	1	1	700
22588.38478	6	1	5	5	2	4	700
22587.74929	8	1	8	7	0	7	700
22586.37552	7	1	6	6	2	5	700
22582.94299	4	2	2	3	2	1	115
22557.89994	6	1	5	6	0	6	700
22532.40838	3	2	1	3	1	2	700
22500.16073	6	2	4	6	2	5	601
22497.26414	3	2	2	3	2	1	115
22495.65550	6	3	4	6	2	5	700
22494.73943	4	2	2	4	2	3	115
22409.05621	3	2	2	4	2	3	115
22253.70269	8	1	8	9	0	9	700
20634.71884	5	1	4	4	1	3	303
20576.15292	2	1	2	1	1	1	303
20493.94634	1	0	1	2	0	2	303
19727.09863	2	2	1	3	1	2	600
19624.67047	5	1	5	6	0	6	600

[18, 40–42]. A full list of energy levels which we regard as suspicious is given in EPAPS [?]. Above  $20\,000\text{ cm}^{-1}$  there are relatively few assigned water transitions and the proportion of mis-assignments became significant. In this region we therefore endeavoured to make re-assignments to increase the data available for the fit. Table II presents 23 transitions reassigned from previous studies of water spectra in the near ultraviolet [42–44]. These



TABLE III: Fitted coefficients,  $c_{i,j,k}$ , of the morphing function, see eq. (2). Dimensions are  $a_0^{-(i+k)}$ .

$i$	$j$	$k$	PES A	PES B
0	0	0	1.000027158917145	0.999990527072135
1	1	0	-0.000770927351806	-0.002771160825579
1	0	1	0.005225529476559	0.007235940923836
2	0	0	-0.005321821288306	-0.006201502857102
3	0	0	0.012313065005899	0.013915771256198
0	0	2	-0.000330530201606	-0.000676732490103
0	0	3	-0.002540182323200	-0.008240369687853
4	0	0	-0.004138553433208	-0.004176466767749
0	2	0	-0.001494291425638	-0.001304789757275
0	3	0	-0.000986086240370	-0.001517064974493
0	4	0	0.001849660194138	0.002075352447003
0	1	1	0.000686890869631	0.004553768345354
2	1	0	0.001271425988015	0.006482689928383
2	0	1	-0.011177721555177	-0.017047069546975
1	2	0	0.001678752458836	0.0015945215629997
0	2	1	-0.000660914325172	-0.000755833001036
1	0	2	0.013905263814636	0.019608670455960
0	1	2	0.018623294327175	0.014305253785881
1	1	1	-0.014679208965237	-0.019900800460336
0	0	4	-0.013979604037784	-0.007462306281290

reassigned transitions yielded new energy levels, given in EPAPS [? ], which were used in the fits.

Table III presents the parameters of the morphing function, eq. (4), for PES A and B. It can be seen that only 20 parameters were adjusted in each case. Although the fits are technically fourth-order ones, only three fourth-order parameters were found to be important and all linear (i.e.  $N = 1$ ) parameters were omitted from the fit. As in each case the resulting potential functions are complicated, a fortran subroutines which calculate the potentials have been included in the EPAPS [? ] archive.

The two fits reproduce the experimental data used with a standard deviation of 0.0999 and 0.1078  $\text{cm}^{-1}$  for fit A and B respectively. These numbers can be compared with the value 3.55  $\text{cm}^{-1}$  obtained using PS's potential and approximately the same data. In practise the assessment of PS is made with slightly fewer energy levels, as detailed in Tables IV. This is because for some high-lying states it proved impossible to reliably match the correct levels in the calculation using PS's surface.

A simple comparison of overall standard deviations is rather crude. A much clearer picture can be obtained by analysing how the various potentials perform as a function of vibrational and rotational excitation. Table IV presents data characterizing the quality of the fit for levels with  $J \leq 10$  for the 105 vibrational states used in our fits. This comparison shows that both our fits perform fairly uniformly throughout the region considered; they both give the poorest results, standard deviation of about 1  $\text{cm}^{-1}$ , for the few high-lying states which combine high stretching excitation with significant bending excitation. These states can only be accurately fitted using higher order terms in the morphing function. At present there is insufficient data on these states to justify including such terms.

In contrast, PS's fit is excellent at low and intermediate levels of vibrational excitation but gives increasingly poor results for the higher vibrational states. By the  $8\nu$  polyad it is performing worse than the *ab initio* calculation upon which it is based. Of course this comparison is somewhat unfair since PS used little data from this high energy region in their fit.

TABLE IV: Summary of fitted energy levels by vibrational band. Band origins and standard deviations are in  $\text{cm}^{-1}$ . Footnotes as for Table V.

Band	Band origin	PS <sup>a</sup>	$N^b$	PES A	$N^c$	PES B
000	00 0	0.0	0.003	80	0.056	80 0.020
010	00 1	1594.746	0.015	81	0.104	81 0.136
020	00 2	3151.630	0.011	81	0.063	81 0.113
100	10 <sup>+</sup> 0	3657.053	0.025	81	0.052	81 0.086
001	10 <sup>-</sup> 0	3755.929	0.015	81	0.088	81 0.033
030	00 3	4666.790	0.046	81	0.028	81 0.083

110	$10^{+1}$	5234.978	0.035	81	0.171	81	0.241
011	$10^{-1}$	5331.265	0.027	81	0.041	81	0.061
040	00 4	6134.015	0.197	81	0.138	81	0.111
120	$10^{+2}$	6775.093	0.023	79	0.119	79	0.188
021	$10^{-1}$	6871.520	0.042	81	0.027	81	0.133
200	$20^{+0}$	7201.540	0.014	81	0.070	81	0.035
101	$20^{-0}$	7249.818	0.023	81	0.059	81	0.048
002	11 0	7445.045	0.065	81	0.055	81	0.046
050	00 5	7542.437	0.084	64	0.248	64	0.148
130	$10^{+3}$	8273.976	0.042	51	0.106	51	0.148
031	$10^{-3}$	8373.853	0.085	81	0.053	81	0.163
210	$20^{+1}$	8761.582	0.067	45	0.093	45	0.129
111	$20^{-1}$	8806.999	0.021	81	0.054	81	0.172
012	11 1	9000.136	0.030	77	0.013	77	0.101
060	00 6	8869.954	0.187	25	0.261	25	0.158
041	$10^{-4}$	9833.585	0.067	63	0.041	63	0.115
220	$20^{+2}$	10284.367	0.042	32	0.018	32	0.019
121	$20^{-2}$	10328.731	0.073	73	0.053	73	0.112
022	11 2	10521.8	0.064	25	0.093	25	0.200
300	$30^{+0}$	10599.686	0.019	72	0.083	72	0.060
201	$30^{-0}$	10613.354	0.038	78	0.020	78	0.091
102	$21^{+0}$	10868.876	0.018	67	0.047	67	0.030
003	$21^{-0}$	11032.406	0.050	75	0.039	75	0.056
070	00 7		0.350	3	0.299	3	0.358
051	$10^{-5}$	11242.8	0.029	22	0.097	22	0.101
230	$20^{+3}$	11767.390	0.111	34	0.107	34	0.121
131	$20^{-3}$	11813.207	0.031	72	0.032	74	0.129
032	11 3	12007.776	0.136	42	0.150	42	0.205
310	$30^{+1}$	12139.315	0.043	67	0.046	68	0.106
211	$30^{-1}$	12151.255	0.046	77	0.098	79	0.217

112	21 <sup>+1</sup>	12407.662	0.037	67	0.022	67	0.076
013	21 <sup>-1</sup>	12565.007	0.014	72	0.032	72	0.096
080	00 8		0.070	1	0.014	1	0.167
160	10 <sup>+6</sup>		0.336	1	0.291	1	0.098
061	10 <sup>-6</sup>	12586.	0.062	8	0.090	8	0.102
240	20 <sup>+4</sup>	13205.1	0.191	39	0.177	39	0.225
141	20 <sup>-4</sup>	13256.2	0.105	40	0.186	40	0.117
042	11 4	13453.6	0.132	35	0.143	35	0.223
320	30 <sup>+2</sup>	13640.7	0.208	61	0.216	61	0.208
221	30 <sup>-2</sup>	13652.656	0.179	69	0.165	69	0.163
122	21 <sup>+2</sup>	13910.896	0.103	62	0.071	62	0.101
023	21 <sup>-2</sup>	14066.194	0.085	71	0.098	71	0.179
400	40 <sup>+0</sup>	13828.277	0.118	77	0.075	77	0.122
301	40 <sup>-0</sup>	13830.938	0.118	80	0.084	80	0.157
202	31 <sup>+0</sup>	14221.161	0.043	74	0.060	74	0.068
103	31 <sup>-0</sup>	14318.812	0.059	74	0.027	74	0.077
004	22 0	14537.504	0.091	68	0.101	68	0.072
170	10 <sup>+7</sup>	13661.1	0.020	1	0.118	1	0.280
071	10 <sup>-7</sup>	13835.372	0.215	5	0.284	5	0.207
151	20 <sup>-5</sup>	14648.2	0.115	19	0.149	19	0.142
330	30 <sup>+3</sup>	15108.239	0.106	29	0.134	29	0.175
231	30 <sup>-3</sup>	15119.028	0.115	67	0.120	67	0.192
132	21 <sup>+3</sup>	15377.7	0.041	17	0.142	17	0.252
033	21 <sup>-3</sup>	15534.709	0.145	61	0.123	61	0.204
410	40 <sup>+1</sup>	15344.503	0.183	65	0.112	65	0.185
311	40 <sup>-1</sup>	15347.956	0.182	70	0.106	70	0.178
212	31 <sup>+1</sup>	15742.795	0.081	57	0.032	57	0.090
113	31 <sup>-1</sup>	15832.765	0.104	68	0.057	68	0.130
340	30 <sup>+4</sup>	16534.3	0.198	29	0.187	29	0.195
241	30 <sup>-4</sup>	16546.3	0.222	33	0.108	33	0.127

142	21 <sup>+4</sup>	16796.0	0.291	35	0.227	35	0.274
043	21 <sup>-4</sup>	16967.5	0.203	18	0.184	18	0.205
420	40 <sup>+2</sup>	16823.	0.431	45	0.153	45	0.170
321	40 <sup>-2</sup>	16821.635	0.674	55	0.227	55	0.238
222	31 <sup>+2</sup>	17227.3	0.213	38	0.112	38	0.130
123	31 <sup>-2</sup>	17312.539	0.233	42	0.167	42	0.188
500	50 <sup>+0</sup>	16898.4	1.070	63	0.104	63	0.128
401	50 <sup>-0</sup>	16898.842	1.188	72	0.130	72	0.179
302	41 <sup>+0</sup>	17458.354	0.889	62	0.119	62	0.113
203	41 <sup>-0</sup>	17495.528	0.824	66	0.145	66	0.151
104	32 <sup>+0</sup>	17748.1	0.377	46	0.173	46	0.264
053	21 <sup>-5</sup>	18350.3	0.101	8	0.059	8	0.036
430	40 <sup>+3</sup>	18271.	4.778	1	0.003	1	0.121
331	40 <sup>-3</sup>	18265.820	0.889	47	0.286	47	0.317
133	31 <sup>-3</sup>	18758.6	0.203	23	0.039	23	0.056
034	22 3	18977.2	0.630	8	0.117	8	0.116
510	50 <sup>+1</sup>	18392.974	0.989	30	0.121	30	0.114
411	50 <sup>-1</sup>	18393.314	1.097	44	0.135	44	0.123
213	41 <sup>-1</sup>	18989.960	0.799	46	0.071	46	0.126
063	21 <sup>-5</sup>	19721.	0.172	3	0.085	3	0.097
341	40 <sup>-4</sup>	19679.1	0.918	30	0.174	30	0.180
520	50 <sup>+2</sup>	19864.	1.349	11	0.525	11	0.547
421	50 <sup>-2</sup>	19863.3	0.527	12	0.673	12	0.687
223	41 <sup>-2</sup>	20442.3	0.394	13	0.213	13	0.219
600	60 <sup>+0</sup>	19781.	8.311	30	0.285	30	0.293
501	60 <sup>-0</sup>	19781.105	8.834	51	0.251	51	0.280
402	51 <sup>+0</sup>	20533.6	3.771	25	0.090	25	0.111
303	51 <sup>-0</sup>	20543.137	4.242	31	0.124	31	0.157
431	50 <sup>-3</sup>	21312.	1.796	11	0.966	11	1.026
610	60 <sup>+1</sup>	21221.569	2.961	8	0.464	8	0.486

511	60 <sup>-1</sup>	21221.828	3.975	22	0.444	22	0.478
115	42 <sup>-1</sup>	22513.	9.423	4	0.215	4	0.220
620	60 <sup>+2</sup>	22631.390	4.248	3	0.837	3	0.845
521	60 <sup>-2</sup>	22629.288	4.535	6	1.022	6	1.030
700	70 <sup>+0</sup>	22529.296	46.484	38	0.135	41	0.134
601	70 <sup>-0</sup>	22529.441	38.013	35	0.112	37	0.152
611	70 <sup>-1</sup>	23940.	24.589	8	0.165	8	0.162
800	80 <sup>+0</sup>		119.669	14	0.213	18	0.131
701	80 <sup>-0</sup>	25120.278	118.330	21	0.189	22	0.134
All Bands			11.678	4902	0.143	4917	0.170

Table V presents a comparison of the various potentials as a function of rotational state  $J$ . Although our fits only used data for  $J = 0, 2$  and  $5$ , they reproduce the data for states with  $J = 0 - 8$  in a uniform fashion. This suggests that our decision not to fit all these  $J$  states simultaneously did not lead to a loss of accuracy. Indeed our fits reproduce all the levels in a uniform fashion as a function of  $J$ , the only exception being for fit A which appears to be less reliable for the highest  $J$ 's. In contrast a superficial inspection of the results obtained with PS's potential would suggest that it is performing significantly better for the high  $J$  states than low  $J$  ones. In practice the lower standard deviation for the high  $J$  levels is simply a reflection of the fact that data on these states is confined to a few, low-lying vibrational states which are well represented by this potential.

#### IV. CONCLUSIONS

We have presented two spectroscopically determined potentials which reliably reproduce the experimental vibration-rotation energy of ground state  $\text{H}_2^{16}\text{O}$  over the entire range for which they have been determined. These potentials differ substantially in the treatment of non-adiabatic effects, particularly those associated with rotation. Fit A omits some terms and is then augmented with a phenomenological term depending on  $J(J + 1)$ ; Fit B is seemingly better grounded in theory but in practice changed the sign of one of the rotational non-adiabatic terms which had previously been obtained *ab initio* [22]. Thus,

TABLE V: Summary of fitted energy levels by rotational state. Standard deviations are in  $\text{cm}^{-1}$ ,

$J$	PS <sup>a</sup>	$N^b$	PES A	$N^c$	PES B
0	4.577	64	0.133	64	0.139
1	10.488	219	0.176	231	0.187
2	11.425	394	0.189	410	0.202
3	15.133	548	0.172	569	0.184
4	14.954	646	0.159	672	0.180
5	16.796	740	0.127	765	0.158
6	9.664	765	0.116	787	0.161
7	7.322	739	0.121	766	0.165
8	6.837	632	0.125	651	0.150
10	0.544	450	0.112	455	0.140
20	0.286	347	0.223	347	0.171
30	0.330	113	0.447	113	0.251

<sup>a</sup>Standard deviation calculated using fitted potential of Partridge and Schwenke (PS) [18].

<sup>b</sup>Number of levels used for the comparison with PS.

<sup>c</sup>Number of levels used for the comparison with PES A and PES B.

neither of these approaches is completely satisfactory and it would appear that more work needs to be done on developing treatments of the rotational non-adiabatic problem.

Our surfaces point to a number of mis-assigned transitions in water spectra over the entire visible region. In this work we have only reanalysed the transitions lying in the blue since the resulting reassignments proved to be important for the quality of the fit. A reanalysis of all water spectra in the visible region is currently being undertaken using the present potentials and a newly determined, high accuracy *ab initio* dipole surface.

### Acknowledgments

We thank David Schwenke for supplying unpublished data on his calculated adiabatic correction. This work was supported by The Royal Society, INTAS, the UK Engineering

- [1] B. M. Dinelli, O. L. Polyansky, and J. Tennyson, *J. Chem. Phys.* **103**, 10433 (1995).
- [2] B. M. Dinelli, S. Miller, and J. Tennyson, *J. Mol. Spectrosc.* **163**, 71 (1994).
- [3] P. C. Gomez and P. Jensen, *J. Mol. Spectrosc.* **185**, 282 (1997).
- [4] V. G. Tyuterev, S. A. Tashkun, P. Jensen, A. Barbe, and T. Cours, *Chem. Phys. Lett.* **198**, 57 (1999).
- [5] J. Zunga, M. Alacid, A. Bastida, F. J. Carvajal, and A. Requena, *J. Mol. Spectrosc.* **195**, 137 (1999).
- [6] V. G. Tyuterev, S. A. Tashkun, and D. W. Schwenke, *Chem. Phys. Lett.* **348**, 223 (2001).
- [7] P. Jensen, R. J. Buenker, J. P. Gu, G. Osmani, and P. R. Bunker, *Can. J. Phys* pp. 641–652 (2001).
- [8] O. L. Polyansky, *J. Molec. Spec.* **112**, 79 (1985).
- [9] S. Carter and N. C. Handy, *J. Chem. Phys.* **87**, 4294 (1987).
- [10] L. Halonen and T. Carrington Jr., *J. Chem. Phys.* **88**, 4171 (1988).
- [11] P. Jensen, *J. Molec. Spec.* **133**, 438 (1989).
- [12] C. D. Paulse and J. Tennyson, *J. Mol. Spectrosc.* **168**, 313 (1994).
- [13] O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **105**, 6490 (1996).
- [14] O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **101**, 7651 (1994).
- [15] P. Jensen, S. A. Tashkun, and V. G. Tyuterev, *J. Mol. Spectrosc.* **168**, 271 (1994).
- [16] A. R. Hoy, I. M. Mills, and G. Strey, *Molec. Phys.* **24**, 1265 (1972).
- [17] D. Xie and G. Yan, *Chem. Phys. Lett.* **248**, 409 (1996).
- [18] H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997).
- [19] J. H. Schryber, O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Mol. Spectrosc.* **185**, 234 (1997).
- [20] J. Tennyson, P. Barletta, M. A. Kostin, O. L. Polyansky, and N. F. Zobov, *Spectrochimica Acta A* **58**, 663 (2002).
- [21] N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, and J. Tennyson, *Chem. Phys. Lett.* **260**, 381 (1996).
- [22] D. W. Schwenke, *J. Phys. Chem. A* **105**, 2352 (2001).



- [23] J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, and P. F. Bernath, *J. Phys. Chem. Ref. Data* **30**, 735 (2001).
- [24] A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, *Chem. Phys. Letts.* **293**, 317 (1998), erratum 312, 613-616 (1999).
- [25] H. M. Quiney, P. Barletta, G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson, *Chem. Phys. Lett.* **344**, 413 (2001).
- [26] P. Pyykkö, K. G. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A* **63**, 024502 (2001).
- [27] B. T. Sutcliffe and J. Tennyson, *Intern. J. Quantum Chem.* **39**, 183 (1991).
- [28] J. Tennyson and B. T. Sutcliffe, *Intern. J. Quantum Chem.* **42**, 941 (1992).
- [29] J. S. Kain, O. L. Polyansky, and J. Tennyson, *Chem. Phys. Letts.* **317**, 365 (2000).
- [30] B. Gazdy and J. M. Bowman, *J. Chem. Phys.* **95**, 6309 (1991).
- [31] M. Meuwly and J. M. Hutson, *J. Chem. Phys.* **110**, 8338 (1999).
- [32] P. Barletta, Ph.D. thesis, University College London (2002).
- [33] A. J. C. Varandas, *J. Chem. Phys.* **105**, 3524 (1996).
- [34] P. Bunker and R. Moss, *Molec. Phys.* **33**, 417 (1977).
- [35] C. Schwartz and R. J. Le Roy, *J. Molec. Spectrosc.* **121**, 420 (1987).
- [36] P. R. Bunker and R. E. Moss, *J. Molec. Spec.* **80**, 217 (1980).
- [37] O. L. Polyansky and J. Tennyson, *J. Chem. Phys.* **110**, 5056 (1999).
- [38] J. Tennyson, J. R. Henderson, and N. G. Fulton, *Computer Phys. Comms.* **86**, 175 (1995).
- [39] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, J. Ramanlal, O. Polyansky, and N. F. Zobov, *Computer Phys. Comm.* (2002).
- [40] O. L. Polyansky, N. F. Zobov, S. Viti, and J. Tennyson, *J. Mol. Spectrosc.* **189**, 291 (1998).
- [41] D. W. Schwenke, *J. Molec. Spec.* **190**, 397 (1998).
- [42] M. Carleer, A. Jenouvrier, A.-C. Vandaele, P. F. Bernath, M. F. Marianne, R. Colin, N. F. Zobov, O. L. Polyansky, J. Tennyson, and V. A. Savin, *J. Chem. Phys.* **111**, 2444 (1999).
- [43] N. F. Zobov, D. Belmiloud, O. L. Polyansky, J. Tennyson, S. V. Shirin, M. Carleer, A. Jenouvrier, A.-C. Vandaele, P. F. Bernath, M. F. Marianne, et al., *J. Chem. Phys.* **113**, 1546 (2000).
- [44] C. Camy-Peyret, J. M. Flaud, J. Y. Mandin, J. P. Chevillard, J. Brault, D. A. Ramsay, M. Vervloet, and J. Chauville, *J. Molec. Spec.* **113**, 208 (1985).