

Spectroscopically determined potential energy surface of H₂¹⁶O up to 25 000 cm⁻¹

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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 nonadiabatic non-Born–Oppenheimer corrections. Fits are made by scaling the starting potential by a morphing function, the parameters of which are optimized. Two fitted potentials are presented which only differ significantly in their treatment of rotational nonadiabatic effects. Energy levels up to 25 468 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 cm⁻¹, and are only slightly worse for $J=20$, for which rotational nonadiabatic effects are significant. The fits showed that around 100 known energy levels are probably the result of misassignments. Analysis of misassigned levels above 20 000 cm⁻¹ leads to the reassignment of 23 transitions. © 2003 American Institute of Physics.

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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 H₃⁺,^{1,2} H₂Te,³ O₃,⁴ CO₂,⁵ H₂S,⁶ and HO₂.⁷ These surfaces are, at least in principle, sufficient to determine all the vibrational and rotational energy levels and wave functions 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 used 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 theory⁸ 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 im-

proved *ab initio* electronic potentials as the starting point. Partridge and Schwenke (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 H₂¹⁶O with an accuracy of 1.17 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 H₃⁺ and its isotopomers.¹ Tests using *ab initio* surfaces suggest that for water, breakdown of the Born–Oppenheimer approximation becomes important if sub 1 cm⁻¹ accuracy is desired.^{20–22}

In this work we use the increased data set of experimentally determined H₂¹⁶O 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*

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TABLE I. Summary of spectroscopically determined H₂¹⁶O potential energy surfaces.

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

^a σ_{vib} is the standard deviation of the fitted vibrational levels in cm⁻¹.

^b N_{vib} is the number of vibrational levels used in the fit.

^c E_{max} is the maximum energy of the fitted vibrational levels in cm⁻¹.

initio potential of PS as a starting point, but augment this potential with *ab initio* estimates of relativistic,^{24,25} adiabatic²² and even quantum electrodynamic²⁶ corrections to the potential. Furthermore, allowance is explicitly made for both vibrational and rotational nonadiabatic 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 H₂¹⁶O.

II. METHOD

All potentials below are functions of the standard bond length, bond angle coordinates of water, (r_1, r_2, θ) . Their equilibrium values r_e and θ_e were taken as 1.809 650 34 a_0 and 1.824 044 93 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 PS¹⁸ 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 ΔB gives the change in the height of the barrier to linearity.

The general form for the fitted potential used by us is

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

where V_{ai} is the *ab initio* starting point, f_{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

$$s_1 = \frac{r_1 + r_2}{2} - r_e, \quad (3)$$

$$s_2 = \cos \theta - \cos \theta_e,$$

$$s_3 = \frac{r_1 - r_2}{2},$$

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

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, ΔV_{ad} . In this work we use the H₂¹⁶O adiabatic correction due to Schwenke²² 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 nonadiabatic 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 midpoint 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 nonadiabatic effects.^{34,35} For water such a formulation was originally presented by Bunker and Moss.³⁶ Here vibrational nonadiabatic effects were included using the two-term correction of Tenynson *et al.*²⁰ which was found to be a good approximation to the full vibrational nonadiabatic treatment of Schwenke.²² This correction to the Born–Oppenheimer nuclear motion Hamiltonian²⁸ 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 $A = -1.0602 \times 1.027 5213 \times 10^{-7}$ and $B = -1.406 2589 \times 10^{-8}$ 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

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

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

A similarly simplified treatment, suggested by Schwenke,²² of his full rotational nonadiabatic calculation is given by adding the following extra term to the standard, Radau bisector, nuclear motion kinetic energy operator:^{27,28}

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

where

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

and the constants ϵ_{ii} , values for which were taken from Schwenke,²² give the magnitude of the rotational nonadiabatic effect.

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

Fit *A* included most of the nonadiabatic corrections described above but omitted both the extra term (7) and the off-diagonal k term in the rotational nonadiabatic 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 nonadia-

batic 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 labeled PES *A* below.

Fit *B* included all nonadiabatic corrections detailed above but used ϵ_{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 ϵ_{ii} are the values given in Table IV of Schwenke.²² The potential resulting from this fit is labeled 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 ΔV_1^{rel} and ΔV_2^{rel} are the first-order²⁴ and second-order²⁵ 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 suite³⁸ 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 oscillatorlike 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 nonadiabatic 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.^{18,40–42} A full list of energy levels which we regard as suspicious is given in EPAPS.⁴³ Above $20\,000 \text{cm}^{-1}$ there are relatively few assigned water transitions and the proportion of misassignments became significant. In this region we therefore endeavoured to make reassignments to increase the data available for the fit. Table II presents 23 transitions reassignment from previous studies of water spectra in the near

TABLE II. Reassigned high-frequency transitions of H₂¹⁶O, data from Refs. 42, 44, and 45. All transitions are from the (000) vibrational state.

ω/cm^{-1}	$J' K'_a K'_c$	$J'' K''_a K''_c$	$v'_1 v'_2 v'_3$
25 184.937 28	6 1 5	5 1 4	701
24 000.632 15	3 2 2	2 2 1	611
22 626.277 72	3 2 1	2 1 2	700
22 606.569 10	6 2 4	5 2 3	601
22 605.603 14	3 2 2	2 1 1	700
22 588.384 78	6 1 5	5 2 4	700
22 587.749 29	8 1 8	7 0 7	700
22 586.375 52	7 1 6	6 2 5	700
22 582.942 99	4 2 2	3 2 1	115
22 557.899 94	6 1 5	6 0 6	700
22 532.408 38	3 2 1	3 1 2	700
22 500.160 73	6 2 4	6 2 5	601
22 497.264 14	3 2 2	3 2 1	115
22 495.655 50	6 3 4	6 2 5	700
22 494.739 43	4 2 2	4 2 3	115
22 409.056 21	3 2 2	4 2 3	115
22 253.702 69	8 1 8	9 0 9	700
20 634.718 84	5 1 4	4 1 3	303
20 576.152 92	2 1 2	1 1 1	303
20 493.946 34	1 0 1	2 0 2	303
19 727.098 63	2 2 1	3 1 2	600
19 624.670 47	5 1 5	6 0 6	600

ultraviolet.^{42,44,45} These reassigned transitions yielded new energy levels, given in EPAPS,⁴³ 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. Fortran subroutines which calculate the potentials have been included in the EPAPS⁴³ archive.

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	1.000 027 158 917 145	0.999 990 527 072 135
1 1 0	-0.000 770 927 351 806	-0.002 771 160 825 579
1 0 1	0.005 225 529 476 559	0.007 235 940 923 836
2 0 0	-0.005 321 821 288 306	-0.006 201 502 857 102
3 0 0	0.012 313 065 005 899	0.013 915 771 256 198
0 0 2	-0.000 330 530 201 606	-0.000 676 732 490 103
0 0 3	-0.002 540 182 323 200	-0.008 240 369 687 853
4 0 0	-0.004 138 553 433 208	-0.004 176 466 767 749
0 2 0	-0.001 494 291 425 638	-0.001 304 789 757 275
0 3 0	-0.000 986 086 240 370	-0.001 517 064 974 493
0 4 0	0.001 849 660 194 138	0.002 075 352 447 003
0 1 1	0.000 686 890 869 631	0.004 553 768 345 354
2 1 0	0.001 271 425 988 015	0.006 482 689 928 383
2 0 1	-0.011 177 721 555 177	-0.017 047 069 546 975
1 2 0	0.001 678 752 458 836	0.015 945 215 629 997
0 2 1	-0.000 660 914 325 172	-0.000 755 833 001 036
1 0 2	0.013 905 263 814 636	0.019 608 670 455 960
0 1 2	0.018 623 294 327 175	0.014 305 253 785 881
1 1 1	-0.014 679 208 965 237	-0.019 900 800 460 336
0 0 4	-0.013 979 604 037 784	-0.007 462 306 281 290

The two fits reproduce the experimental data used with a standard deviation of 0.0999 and 0.1078 cm⁻¹ for fit A and B, respectively. These numbers can be compared with the value 3.55 cm⁻¹ obtained using PS's potential and approximately the same data. In practice the assessment of PS is made with slightly fewer energy levels, as detailed in Table 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 analyzing 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 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 ν 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 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 H₂¹⁶O over the entire range for which they have been determined. These potentials differ substantially in the treatment of nonadiabatic 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 nonadiabatic terms which had previously been obtained *ab initio*.²² Thus, neither of these approaches is com-

TABLE IV. Summary of fitted energy levels by vibrational band. Band origins and standard deviations are in cm^{-1} .

Band	Band origin	PS ^a	N ^b	PES A	N ^c	PES B	Band	Band origin	PS ^a	N ^b	PES A	N ^c	PES B		
000	00 0	0.0	0.003	80	0.056	80	0.020	170	10 ⁺ 7	13 661.1	0.020	1	0.118	1	0.280
010	00 1	1594.746	0.015	81	0.104	81	0.136	071	10 ⁻ 7	13 835.372	0.215	5	0.284	5	0.207
020	00 2	3151.630	0.011	81	0.063	81	0.113	151	20 ⁻ 5	14 648.2	0.115	19	0.149	19	0.142
100	10 ⁺ 0	3657.053	0.025	81	0.052	81	0.086	330	30 ⁺ 3	15 108.239	0.106	29	0.134	29	0.175
001	10 ⁻ 0	3755.929	0.015	81	0.088	81	0.033	231	30 ⁻ 3	15 119.028	0.115	67	0.120	67	0.192
030	00 3	4666.790	0.046	81	0.028	81	0.083	132	21 ⁺ 3	15 377.7	0.041	17	0.142	17	0.252
110	10 ⁺ 1	5234.978	0.035	81	0.171	81	0.241	033	21 ⁻ 3	15 534.709	0.145	61	0.123	61	0.204
011	10 ⁻ 1	5331.265	0.027	81	0.041	81	0.061	410	40 ⁺ 1	15 344.503	0.183	65	0.112	65	0.185
040	00 4	6134.015	0.197	81	0.138	81	0.111	311	40 ⁻ 1	15 347.956	0.182	70	0.106	70	0.178
120	10 ⁺ 2	6775.093	0.023	79	0.119	79	0.188	212	31 ⁺ 1	15 742.795	0.081	57	0.032	57	0.090
021	10 ⁻ 1	6871.520	0.042	81	0.027	81	0.133	113	31 ⁻ 1	15 832.765	0.104	68	0.057	68	0.130
200	20 ⁺ 0	7201.540	0.014	81	0.070	81	0.035	340	30 ⁺ 4	16 534.3	0.198	29	0.187	29	0.195
101	20 ⁻ 0	7249.818	0.023	81	0.059	81	0.048	241	30 ⁻ 4	16 546.3	0.222	33	0.108	33	0.127
002	11 0	7445.045	0.065	81	0.055	81	0.046	142	21 ⁺ 4	16 796.0	0.291	35	0.227	35	0.274
050	00 5	7542.437	0.084	64	0.248	64	0.148	043	21 ⁻ 4	16 967.5	0.203	18	0.184	18	0.205
130	10 ⁺ 3	8273.976	0.042	51	0.106	51	0.148	420	40 ⁺ 2	16 823.0	0.431	45	0.153	45	0.170
031	10 ⁻ 3	8373.853	0.085	81	0.053	81	0.163	321	40 ⁻ 2	16 821.635	0.674	55	0.227	55	0.238
210	20 ⁺ 1	8761.582	0.067	45	0.093	45	0.129	222	31 ⁺ 2	17 227.3	0.213	38	0.112	38	0.130
111	20 ⁻ 1	8806.999	0.021	81	0.054	81	0.172	123	31 ⁻ 2	17 312.539	0.233	42	0.167	42	0.188
012	11 1	9000.136	0.030	77	0.013	77	0.101	500	50 ⁺ 0	16 898.4	1.070	63	0.104	63	0.128
060	00 6	8869.954	0.187	25	0.261	25	0.158	401	50 ⁻ 0	16 898.842	1.188	72	0.130	72	0.179
041	10 ⁻ 4	9833.585	0.067	63	0.041	63	0.115	302	41 ⁺ 0	17 458.354	0.889	62	0.119	62	0.113
220	20 ⁺ 2	10 284.367	0.042	32	0.018	32	0.019	203	41 ⁻ 0	17 495.528	0.824	66	0.145	66	0.151
121	20 ⁻ 2	10 328.731	0.073	73	0.053	73	0.112	104	32 ⁺ 0	17 748.1	0.377	46	0.173	46	0.264
022	11 2	10 521.8	0.064	25	0.093	25	0.200	053	21 ⁻ 5	18 350.3	0.101	8	0.059	8	0.036
300	30 ⁺ 0	10 599.686	0.019	72	0.083	72	0.060	430	40 ⁺ 3	18 271.0	4.778	1	0.003	1	0.121
201	30 ⁻ 0	10 613.354	0.038	78	0.020	78	0.091	331	40 ⁻ 3	18 265.820	0.889	47	0.286	47	0.317
102	21 ⁺ 0	10 868.876	0.018	67	0.047	67	0.030	133	31 ⁻ 3	18 758.6	0.203	23	0.039	23	0.056
003	21 ⁻ 0	11 032.406	0.050	75	0.039	75	0.056	034	22 3	18 977.2	0.630	8	0.117	8	0.116
070	00 7		0.350	3	0.299	3	0.358	510	50 ⁺ 1	18 392.974	0.989	30	0.121	30	0.114
051	10 ⁻ 5	11 242.8	0.029	22	0.097	22	0.101	411	50 ⁻ 1	18 393.314	1.097	44	0.135	44	0.123
230	20 ⁺ 3	11 767.390	0.111	34	0.107	34	0.121	213	41 ⁻ 1	18 989.960	0.799	46	0.071	46	0.126
131	20 ⁻ 3	11 813.207	0.031	72	0.032	74	0.129	063	21 ⁻ 5	19 721.0	0.172	3	0.085	3	0.097
032	11 3	12 007.776	0.136	42	0.150	42	0.205	341	40 ⁻ 4	19 679.1	0.918	30	0.174	30	0.180
310	30 ⁺ 1	12 139.315	0.043	67	0.046	68	0.106	520	50 ⁺ 2	19 864.0	1.349	11	0.525	11	0.547
211	30 ⁻ 1	12 151.255	0.046	77	0.098	79	0.217	421	50 ⁻ 2	19 863.3	0.527	12	0.673	12	0.687
112	21 ⁺ 1	12 407.662	0.037	67	0.022	67	0.076	223	41 ⁻ 2	20 442.3	0.394	13	0.213	13	0.219
013	21 ⁻ 1	12 565.007	0.014	72	0.032	72	0.096	600	60 ⁺ 0	19 781.0	8.311	30	0.285	30	0.293
080	00 8		0.070	1	0.014	1	0.167	501	60 ⁻ 0	19 781.105	8.834	51	0.251	51	0.280
160	10 ⁺ 6		0.336	1	0.291	1	0.098	402	51 ⁺ 0	20 533.6	3.771	25	0.090	25	0.111
061	10 ⁻ 6	12 586.0	0.062	8	0.090	8	0.102	303	51 ⁻ 0	20 543.137	4.242	31	0.124	31	0.157
240	20 ⁺ 4	13 205.1	0.191	39	0.177	39	0.225	431	50 ⁻ 3	21 312.0	1.796	11	0.966	11	1.026
141	20 ⁻ 4	13 256.2	0.105	40	0.186	40	0.117	610	60 ⁺ 1	21 221.569	2.961	8	0.464	8	0.486
042	11 4	13 453.6	0.132	35	0.143	35	0.223	511	60 ⁻ 1	21 221.828	3.975	22	0.444	22	0.478
320	30 ⁺ 2	13 640.7	0.208	61	0.216	61	0.208	115	42 ⁻ 1	22 513.0	9.423	4	0.215	4	0.220
221	30 ⁻ 2	13 652.656	0.179	69	0.165	69	0.163	620	60 ⁺ 2	22 631.390	4.248	3	0.837	3	0.845
122	21 ⁺ 2	13 910.896	0.103	62	0.071	62	0.101	521	60 ⁻ 2	22 629.288	4.535	6	1.022	6	1.030
023	21 ⁻ 2	14 066.194	0.085	71	0.098	71	0.179	700	70 ⁺ 0	22 529.296	46.484	38	0.135	41	0.134
400	40 ⁺ 0	13 828.277	0.118	77	0.075	77	0.122	601	70 ⁻ 0	22 529.441	38.013	35	0.112	37	0.152
301	40 ⁻ 0	13 830.938	0.118	80	0.084	80	0.157	611	70 ⁻ 1	23 940.0	24.589	8	0.165	8	0.162
202	31 ⁺ 0	14 221.161	0.043	74	0.060	74	0.068	800	80 ⁺ 0		119.669	14	0.213	18	0.131
103	31 ⁻ 0	14 318.812	0.059	74	0.027	74	0.077	701	80 ⁻ 0	25 120.278	118.330	21	0.189	22	0.134
004	22 0	14 537.504	0.091	68	0.101	68	0.072	All bands			11.678	4902	0.143	4917	0.170

^aStandard deviation calculated using fitted potential of PS (Ref. 18).^bNumber of levels used for the comparison with PS.^cNumber of levels used for the comparison with PES A and PES B.

pletely satisfactory and it would appear that more work needs to be done on developing treatments of the rotational nonadiabatic problem.

Our surfaces point to a number of misassigned transitions in water spectra over the entire visible region. In this work we have only reanalyzed 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.

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TABLE V. Summary of fitted energy levels by rotational state. Standard deviations are in cm⁻¹.

<i>J</i>	PS ^a	<i>N</i> ^b	PES A	<i>N</i> ^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

^aStandard deviation calculated using fitted potential of PS (Ref. 18).^bNumber of levels used for the comparison with PS.^cNumber of levels used for the comparison with PES A and PES B.

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