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The ground-state potential energy surface of water: barrier to linearity and its effect on the vibration–rotation levels

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Abstract

The major factor determining the accuracy of ro-vibrational spectra of the water molecule is the accuracy of the underlying potential energy surface (PES). We discuss improving the ab initio PES by introducing a correction to represent, accurately, the change in potential from equilibrium to linear geometries. We show the improvements which this has on calculated vibrational band origins and rotational energy levels by comparison with experimental data. We predict a barrier to linearity of $11\,105 \pm 5$ cm^{-1}, consistent with, but more accurate than, recent studies. This potential provides the optimum starting point for a proper fit of the PES. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The ro-vibrational spectrum of water has been intensely studied for decades as it is important for many applications. Interpretation of the spectra is particularly important for our understanding of the transmission of solar radiation in the Earth's atmosphere, as well as the atmosphere of cool stars and brown dwarfs. Although considerable work has been done on this molecule, much of the observational data still remain unassigned.

For example, Wallace et al. [1–3] published a series of atlases of sunspot spectra. While some lines in these sunspot spectra were easily assigned, large portions due to water [4] were originally considered unassignable. However, by shifting the theoretical method used to analyse these spectra from perturbative expansions of effective Hamiltonians to variational calculations in combination with accurate first principles formulation of the problem, it has become possible to start assigning these spectra [5]. Nonetheless, in the most congested regions of the spectra, only the strongest transitions, about 15% of the total, have thus far been assigned [5,6]. The remaining lines are also due to water, and the overall accuracy of the variational calculations must be further improved in order to assign these lines.

To predict accurate rotation–vibration energies of the water molecule, one must start with a highly accurate potential energy surface (PES). The best available ab initio PESs can predict the vibrational fundamentals of water to within about 2 cm^{-1} [7,8], an error which increases significantly for higher band origins. One method of improving the poten-

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tials is to perform iterative fits to spectroscopic data. This method produces effective PESs which can reproduce the known data to high accuracy [7,11,12]. However, our experience shows that such surfaces extrapolate to higher vibration–rotation energy levels significantly worse than a completely ab initio approach [9,10]. This behaviour can be ascribed to uncertainty in the exact model being used for the fit and, in particular, to problems with the Born–Oppenheimer approximation.

Improving the accuracy of a PES involves taking all physically significant factors into account. Recently Császár et al. [13] performed a comprehensive and systematic study of barriers to internal rotation in a number of molecules. Water was the smallest system considered but, perhaps somewhat surprisingly, the barrier to linearity in water proved to be one of the most difficult to determine accurately. Their calculated barrier height, $11\,046 \pm 70$ cm^{-1}, showed the importance of the electronic relativistic correction and, more seriously, the correlation energy displayed very slow convergence with respect to basis set expansion.

Tarczay et al. [14] followed up this work by performing an even more detailed ab initio quantum-chemical investigation of the barrier height in water. Their investigation involved calculations using a very large one-particle basis set for the calculation of electron correlation, the 443 function aug-cc-pV6Z basis set, as well as explicitly correlated wavefunctions. Despite the sophistication of their treatment, they were unable to get a tightly converged estimate of the barrier height. Their best estimate was $11\,127 \pm 35$ cm^{-1}. It appears unlikely that the results of Tarczay et al. will be improved upon using conventional electronic structure calculation methodology [15].

The best available ab initio ground-state PES for water is due to Partridge and Schwenke [7]. Their calculation gives a barrier height of 11 155 cm^{-1}, which becomes 11 192 cm^{-1} when an allowance is made for relativistic and adiabatic corrections. It is notable that Partridge and Schwenke found it much more difficult to converge the angular rather than the radial parts of their potential; specific errors are discussed below. It has long been known that ab initio methods perform less well for the bending than the stretching motions of water [19]. A summary of different predicted barrier heights obtained by various authors is presented in Table 1.

Császár et al. [18] investigated how the first-order electronic relativistic correction influences the spectroscopic properties of water. Their computed relativistic correction surface raised the barrier height by 50 cm^{-1}. They found that the relativistic correction was more significant than the Born–Oppenheimer diagonal correction (BODC) investigated by Zobov et al. [16]. Quiney et al. [17] also investigated the significance of the relativistic correction using a full Dirac treatment and obtained results are in good agreement with Császár et al. [18].

One important effect of the relativistic correction of Császár et al. [18] was that it led to a major improvement in the predicted stretching fundamental and overtone frequencies. This improvement was achieved at the expense of the bending fundamental

Table 1
A comparison of predicted barriers to linearity for water ($H_2{}^{16}O$ when adiabatic effects are considered)

	Barrier height	Comments
Carter and Handy [28]	11 493 cm^{-1}	spectroscopic empirical
Jensen [29]	11 246 cm^{-1}	spectroscopic empirical
Polyansky et al. [12]	10 966 cm^{-1}	spectroscopic empirical
Lanquetin et al. [30]	11 154 cm^{-1}	effective Hamiltonian
Partridge and Schwenke [7]	11 155 cm^{-1}	ab initio
Partridge and Schwenke [7]	11 128 cm^{-1}	spectroscopic empirical
Partridge and Schwenke, adiabatic, relativistic [18]	11 192 cm^{-1}	ab initio
Császár et al. [13]	$11\,046 \pm 70$ cm^{-1}	extrapolated ab initio
Tarczay et al. [14]	$11\,127 \pm 35$ cm^{-1}	high accuracy ab initio
This work	$11\,105 \pm 5$ cm^{-1}	corrected ab initio

and overtones which were severely overestimated. As demonstrated below, these frequencies are very sensitive to the height of the barrier to linearity used in any calculation. There is still rather limited spectroscopic data available on higher bending overtones of water. The $5\nu_2$ and $6\nu_2$ band origins have only recently been measured correctly [20,21] and a few levels in combination states involving seven quanta of bend have also recently been assigned [9,22]. Further progress on assigning water spectra relies on improved predictions for the bending states yet to be assigned. Similarly, rotationally excited states with high values of the K_a quantum number are well known to be difficult to analyse [23]. As shown below, these states are also very sensitive to any treatment of the bending potential and any improved analysis of highly rotationally excited states require improvements in the treatment of this coordinate.

In the absence of a fully converged ab initio potential and given the difficulty of extrapolating potentials fitted to limited observed data, we have attempted an intermediate course. In this work, we augment the best available ab nitio model for water [7,10] with a correction to the bending potential. This leads to an order of magnitude improvement in the predicted vibrational band origins and thus gives a good starting point for future spectroscopic analysis.

2. Calculations

To test the various PESs considered, nuclear motion calculations were performed for the $H_2{}^{16}O$ isotopomer of water for which extensive spectroscopic data is available. Experimental vibrational band origins were taken from the Hitran database [24] and augmented by more recent data [9,20–22]. Rotationally excited levels were taken from the work of Flaud et al. [25] and Polyansky et al. [26]. A standard deviation was calculated for both the rotational and vibrational levels. σ_{vib} is the standard deviation of the observed minus calculated values for all the $J=0$, even parity energy levels for which experimental data is available. σ_{rot} is the standard deviation of the observed minus calculated values of $J=20$ vibrational ground state.

Nuclear motion calculations were performed using the DVR3D program suite [27] and previously optimised basis sets [11]. The initial PES used was the Born–Oppenheimer $V5z+\Delta V^{\mathrm{core}}$ potential due to Partridge and Schwenke [7] which is the best available ab initio potential to date. This potential was augmented by the adiabatic correction of Zobov et al. [16] and the relativistic correction of Császár et al. [18]. Following Zobov et al., further allowance for failure of the Born–Oppenheimer approximation was made by using hydrogenic masses midway between the nuclear and atomic value.

A number of different correction potentials were considered. They are summarized in Table 2, and plotted in Fig. 1. In defining these potentials, $\Delta V(\theta)$, a number of criteria were used. First we restricted the study to potentials which depended on the HOH bond angle θ only. Second, we are interested in the shift in the height of the barrier to linearity defined by $B=V(R_\pi,R_\pi,\pi)-V(R_e,R_e,\theta_e)$, where for the model used here $\theta_e=1.82$ radians, the equilibrium OH separation is $R_e=1.81\ a_o$ and the saddle point at linearity occurs for $R_\pi=1.76\ a_o$. A third criterion

$$\left.\frac{\partial\Delta V}{\partial\theta}\right|_{\theta=\pi}=0 \qquad (1)$$

was introduced during the course of the study. We define, for the purpose of this Letter, the correction to the barrier height as $\Delta B=\Delta V(\pi)-\Delta V(\theta_e)$, and the zero of energy by $\Delta V(\theta_e)=0$.

Initially a linear function in θ, shown in Table 2, was added to the barrier. The first correction to the barrier height tried was the difference between the barrier height predicted by Tarczay et al. [14] and the barrier height for our PES, i.e. 11 127–11 192 cm^{-1}. ΔB was successively altered to find the optimum value, to within 5 cm^{-1}, based on the overall standard deviation for both the vibrational and rotational motion (σ_{vib}, σ_{rot}). This gave an optimum value of $\Delta B=-115\ \mathrm{cm}^{-1}$ (see Table 2) which greatly improved the standard deviation for the vibrational motion, σ_{vib}. The linear barrier correction worsens the value of σ_{rot}.

Partridge and Schwenke (PS) [7] discuss convergence error with basis set size as a function of angle. They assume that the energies converge logarithmically and extrapolate the energies to the complete basis set (CBS) limit for the three largest basis sets used. This extrapolation value minus the energy

Table 2
Different functions, $\Delta V(\theta)$, used to correct the angular potential. Also given are the standard deviation of the vibrational modes, σ_{vib}, the standard deviation of the rotational levels, σ_{rot}, and the correction to the barrier height, ΔB

	$\Delta V(\theta)$	$\sigma_{\mathrm{vib}}/\mathrm{cm}^{-1}$	$\sigma_{\mathrm{rot}}/\mathrm{cm}^{-1}$	$\Delta B/\mathrm{cm}^{-1}$
	0	8.5	4.5	[11 192][a]
Linear	$\frac{\Delta B(\theta-\theta_e)}{\pi-\theta_e}$	4.8	5.9	−115
Quadratic	$\frac{\Delta B(\theta^2-\theta_e^2)}{\pi^2-\theta_e^2}$	3.5	2.4	−115
Cubic	$\frac{\Delta B(\theta^3-\theta_e^3)}{\pi^3-\theta_e^3}$	3.0	0.4	−115
Gaussian	$\Delta B\left\{\exp\left[\frac{-\pi(\theta-\pi)^2}{\theta_e}\right]-\exp\left[\frac{-\pi(\theta_e-\pi)^2}{\theta_e}\right]\right\}$	2.0	1.6	−97
Sine[b]	$E\sin^2\left[\frac{\pi(\theta-\theta_e)}{2\theta_e}\right]\ \theta \leqslant \theta_e$	3.7	1.5	−90
	$\Delta B\sin^2\left[\frac{\pi(\theta-\theta_e)}{2(\pi-\theta_e)}\right]\ \theta \geqslant \theta_e$			
Final[c]	$F\frac{(\theta^3-\theta_e^3)}{(\theta_e^3-\pi^3)}+G\frac{(\theta^5-\theta_e^5)}{(\theta_e^5-\pi^5)}-(\Delta B+F+G)\frac{(\theta^2-\theta_e^2)}{(\theta_e^2-\pi^2)}$	1.3	0.3	−87.5

[a] Actual barrier height B when $\Delta V(\theta)=0$.
[b] $E=-22\ \mathrm{cm}^{-1}$.
[c] $F=879.7\ \mathrm{cm}^{-1}$, $G=-381.1\ \mathrm{cm}^{-1}$.

estimate gives an approximate convergence error in the bending modes. These points are plotted in Fig. 1. They give an indication of the shape of the function required and acted as a starting point for testing further functions.

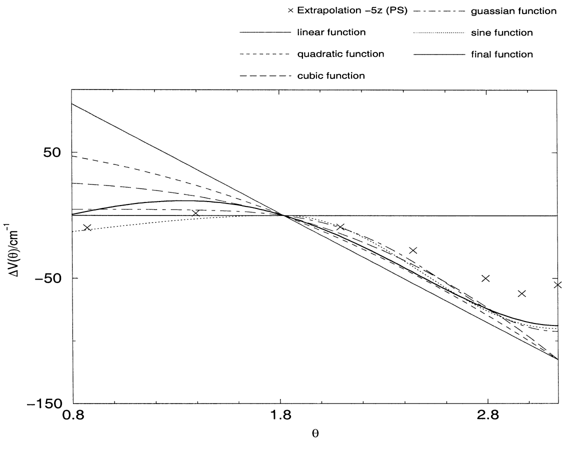

Fig. 1. Functions, $\Delta V(\theta)$, used to model the correction to the barrier height. Solid line, linear function; dashed line, quadratic function; long-dashed line, cubic function; dot-dashed line, Gaussian function; dotted line, sine function. The dark solid line is the final function. ‘X’ denotes errors estimated by extrapolation from their cc-pV5Z basis by Partridge and Schwenke [7].

The second function tested was a quadratic in θ and gave $\Delta B = -115\ \mathrm{cm}^{-1}$. This further reduces the errors in the vibrational band origins and also significantly improves the results for the rotational energy levels. It is instructive to ask why the quadratic function, rather than the linear one, improves the rotational results. This is because the correction for $\theta < \theta_e$ is much smaller. The linear correction over-corrects the potential in this region.

The improved effect of the quadratic correction suggested that a cubic function might perform even better. The results obtained with a cubic correction are indeed an improvement, especially for the rotational levels. The improved rotational results are almost certainly because the functional form has a shallower gradient at θ_e.

The experimental data being used to test our value of ΔB is not directly sensitive to the value of the potential at $\theta = \pi$. It was therefore considered necessary to force the correction to the barrier to behave correctly at $\theta = \pi$ and have a zero differential (Eq. (1). The zero differential property and the PS’s convergence error indicate that either a sine function or a Gaussian function would model the shape successfully. The optimum sine function and Gaussian functions are summarised in Table 2. The results for the Gaussian function, with $\Delta B = -97$ cm^{-1}, gave a further improvement to the vibrations.

The optimum sine function involves a two-parameter fit. The first parameter is ΔB and the second is a parameter to define where the curve crosses the $\theta = 0$ axis. The second parameter was altered to optimise the gradient of the curve at $\theta < \theta_e$. This optimum sine function has a notably smaller ΔB, of 90 cm^{-1}. However, if the steepest gradient on the curve was extrapolated with a straight line, the barrier height would be in agreement with the previous functions, of around 115 cm^{-1}. The results for this function are good for vibrations but less so for rotations. This is found to be because the gradient of the curve, at angles just less than θ_e, is too shallow.

After considerable manipulation of the above functions the shape of the function and its effect on the different motions of the water molecule became well understood and therefore a final function could be chosen.

The final function is also a two-parameter fit, similar to the sine function, where the first parameter is ΔB and the second is a parameter to define where the curve crosses the $\theta = 0$ axis, to optimise the gradient at $\theta < \theta_e$. The final function was forced to have a zero differential at π.

The region $\theta > \theta_e$ particularly effects the vibrational modes of water; water is anharmonic and vibrates considerably more in this region as the repulsive force between the hydrogen atoms is small. In this region the Gaussian had the best value of σ_{vib} and guided the shape of the final curve at $\theta_e < \theta$.

The cubic function had the best standard deviation for the rotations and so the second parameter was varied to have a similar gradient at just less than θ_e.

The final function, given in Table 2, optimised σ_{vib} and σ_{rot} for the water molecule. The final correction to the barrier height for the chosen function is -87 cm^{-1} optimised to the nearest wavenumber. A deviation of 5 cm^{-1} either side makes an appreciable difference to the results. This prediction, therefore, of the barrier height is significantly more accurate than previous predictions, and is also shown in Table 1. Confidence in this value is given by the observation that our preliminary studies arrived at the same value despite using less accurate versions of the starting potential.

The effect on the vibrational band origins of including the final correction to the full ab initio potential is demonstrated in Table 3. These results show clearly how the corrected barrier corrects for the errors in the bending modes.

Table 4 shows $J = 20$ rotational energy levels for the ground vibrational state, with and without the

Table 3
Band origins, in cm^{-1}, for the $H_2{}^{16}O$, even parity only. Results, calculated using (a) Born–Oppenheimer of Partridge and Schwenke [7], (b) with adiabatic and relativistic corrections added [16] and (c) with the addition of our final angular correction, are given as observed − calculated

	Obs.	*a*	*b*	*c*
(010)	1594.75	−2.65	−3.44	−0.10
(020)	3151.63	−5.12	−6.86	−0.07
(100)	3657.05	−3.49	−0.62	−0.85
(030)	4666.80	−7.53	−10.43	0.04
(110)	5235.00	−6.20	−4.13	−1.06
(040)	6134.03	−9.90	−14.26	0.26
(120)	6775.10	−8.64	−7.50	−1.06
(200)	7201.54	−6.38	−0.70	−1.28
(002)	7445.07	−4.89	0.70	−0.86
(050)	7542.39	−12.39	−18.70	0.57
(130)	8273.98	−11.06	−11.07	−1.08
(210)	8761.59	−9.07	−4.18	−1.50
(060)	8870.54	−14.87	−23.98	1.39
(012)	9000.14	−7.50	−2.57	−1.01
(220)	10284.37	−11.39	−7.41	−1.50
(022)	10524.3	−7.5	−3.4	1.30
(300)	10599.69	−8.20	−0.19	−0.96
(102)	10868.88	−8.81	−0.33	−1.66
(310)	12139.2	−10.9	−3.3	−1.24
(112)	12407.64	−11.53	−4.38	−1.85
(240)	13205.1	−16.0	−14.5	−1.42
(042)	13453.7	−14.8	−13.0	−1.40
(320)	13640.8	−13.0	−6.4	−0.79
(170)	13661.3	−19.7	−27.6	0.45
(202)	13828.28	−9.43	1.58	−0.06
(122)	13910.90	−13.82	−6.99	−1.91
(400)	14221.16	−12.00	−0.71	−1.97
(004)	14537.51	−9.18	2.0	−0.97
(330)	15108.24	−15.11	−9.21	−1.26
(212)	15344.50	−12.02	−1.89	−0.19
(410)	15742.80	−14.60	−4.11	−2.12
(222)	16825.23	−12.25	−3.36	1.79
(302)	16898.4	−10.6	2.3	1.30
(420)	17227.70	−16.36	−6.86	−1.68
(104)	17458.30	−13.38	0.56	−1.06
(500)	17748.07	−13.06	0.96	−1.46
(312)	18392.98	−12.28	−0.14	1.85
	σ_{vib}	10.63	8.48	1.25

Table 4

Rotational term values, in cm^{-1}, for the vibrational ground state of $H_2{}^{16}O$. Results, calculated using (a) Born–Oppenheimer of Partridge and Schwenke [7], (b) with adiabatic and relativistic corrections added [16] and (c) with the addition of our final angular correction, are given as observed − calculated

	Obs.	*a*	*b*	*c*
20_{020}	4048.25	−0.53	0.30	0.19
20_{119}	4412.32	−0.57	0.33	0.22
20_{218}	4738.62	−0.66	0.23	0.26
20_{317}	5031.80	−0.80	0.04	0.10
20_{416}	5292.10	−0.99	−0.31	0.32
20_{615}	5527.05	−1.08	−0.45	0.35
20_{614}	5680.79	−1.69	−2.06	0.44
20_{813}	5947.33	−1.00	0.05	0.37
20_{812}	5966.83	−1.27	−1.70	0.39
20_{1011}	6407.08	−0.59	1.70	0.29
20_{1010}	6407.45	−0.60	1.68	0.29
20_{129}	6935.43	−0.24	3.39	0.20
20_{128}	6935.44	−0.24	3.39	0.20
20_{147}	7507.58	−0.03	4.91	0.10
20_{146}	7507.58	−0.03	4.91	0.10
20_{165}	8100.30	−0.05	6.30	0.00
20_{164}	8100.30	−0.05	6.30	0.00
20_{183}	8691.92	−0.06	7.51	−0.17
20_{182}	8691.92	−0.06	7.51	−0.17
20_{201}	9257.41	−0.42	8.49	−0.48
20_{200}	9257.41	−0.42	8.49	−0.48
	σ_{rot}	0.71	4.48	0.29

correction to the barrier. Results obtained for the (010) vibrational levels are very similar. For higher vibrational energy levels the data for $J = 20$ is limited to low K_a. The overall improvement is apparent, although there is still an increase in error with increasing K_a.

Additional calculations were performed for HDO, HTO, D_2O, and T_2O. The vibrational band origins predicted using our final potential gave errors similar to those for H_2O, meaning that this potential appears to have solved the isotopomer problem.

3. Discussion and conclusion

The results show, conclusively, that the barrier height for the PES of water by Partridge and Schwenke [7] augmented by the adiabatic and the relativistic correction is not yet accurately defined. This potential needs further corrections to account for the errors in the bending modes. It has been shown that a careful choice of a simple correcting function significantly improves the bending modes and thus the overall accuracy to which both the vibrationally and rotationally excited levels are reproduced. Of course it is not possible to prove that the adjusting function we have chosen is definitive and we would make no such claim.

As the major error in the vibrational band origins in the original potential is in the bending motion, once correction due to the electronic relativistic motion has been included. It would seem obvious that an angular correction would automatically improve things. However the situation is more complicated as the stretching and bending motions in water are never entirely independent. Thus our angular function is one which does not significantly effect the stretches but improves the bends. It can be seen from Fig. 1 that this function is similar in shape to, but about 50% larger than, the basis set truncation error estimated by Partridge and Schwenke [7] as part of their ab initio study. Our function will thus act as a guide to how future ab initio surfaces should be improved. We note, however, that such studies would also automatically include any bend-stretch coupling.

It can be seen from Table 3 that the predictions for some of the pure stretches are made a little worse by the addition of the final function. However, the overall errors are considerably more uniform and the prediction of the band origins is very much improved. The improved uniformity of the error in the bending and stretching modes significantly improves the extrapolation power of the potential.

The same carefully chosen function also greatly improves the predictions for the rotational term values. For the rotational energy levels there is still a residual, gradual increase in error with increased K_a. This corrected potential should provide a good starting point for future fitted potentials.

Our overall barrier to linearity is found to be $11\,105 \pm 5$ cm^{-1}. This predicted barrier height is in good agreement with the most recent predictions by other authors. It is within the error bars of the prediction of Császár et al. [13] of $11\,046 \pm 70$ cm^{-1} and also that of Tarczay et al. [14] of $11\,127 \pm 35$ cm^{-1}. However, our prediction of the overall barrier height has a greatly reduced uncertainty.

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