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Calculation of Rotation–Vibration Energy Levels of the Water Molecule with Near-Experimental Accuracy Based on an ab Initio Potential Energy Surface

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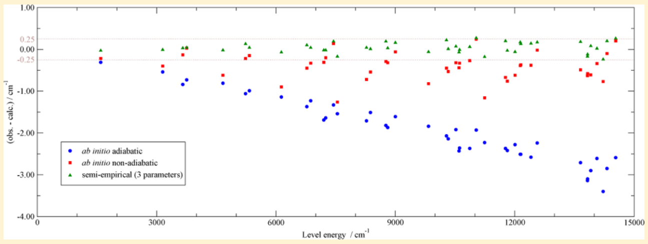
Ⓢ *Supporting Information*

ABSTRACT: A recently computed, high-accuracy ab initio Born–Oppenheimer (BO) potential energy surface (PES) for the water molecule is combined with relativistic, adiabatic, quantum electrodynamics, and, crucially, nonadiabatic corrections. Calculations of ro-vibrational levels are presented for several water isotopologues and shown to have unprecedented accuracy. A purely ab initio calculation reproduces some 200 known band origins associated with seven isotopologues of water with a standard deviation (σ) of about 0.35 cm^{-1}. Introducing three semiempirical scaling parameters, two affecting the BO PES and one controlling nonadiabatic effects, reduces σ below 0.1 cm^{-1}. Introducing one further rotational nonadiabatic parameter gives σ better than 0.1 cm^{-1} for all observed ro-vibrational energy levels up to $J = 25$. We conjecture that the energy levels of closed-shell molecules with roughly the same number of electrons as water, such as NH_3, CH_4, and H_3O^+, could be calculated to this accuracy using an analogous procedure. This means that near-ab initio calculations are capable of predicting transition frequencies with an accuracy only about a factor of 5 worse than high resolution experiments.



■ INTRODUCTION

It has been common practice since at least the 1960s[1−3] to refer to the results of electronic structure calculations as being of chemical accuracy when the error on energy differences is of the order of 1 kcal/mol (~1 mE_h). The rationale behind this definition is that calculations having this accuracy can be reliably used for computing quantities of thermochemical interest such as enthalpies of formations. The term spectroscopic accuracy has also been used for a long time[4] with various definitions and, starting from about the 1990s, has come to refer unequivocally to an accuracy of 1 cm^{-1} (~5 μE_h).[5] Császár et al.[6] have introduced the term hyperfine accuracy to refer to an accuracy of 1 nE_h (~2×10^{-4} cm^{-1}), but currently this degree of accuracy is achievable ab initio only for one- and two-electron diatomics such as H_2^+,[7] H_2,[8,9] and HeH^+.[10] Typical experimental accuracies of high-resolution spectroscopy are usually far higher than spectroscopic accuracy of 1 cm^{-1} ; in the case of the main isotopologue of the water molecule, studies in the terahertz region of rotational transitions can reach extremely high accuracies of 10^{-6} to 10^{-9} cm^{-1} and are capable of fully resolving hyperfine structures.[11−13] Routine measurements of rotational–vibrational lines usually claim uncertainties of about 10^{-3} cm^{-1},[14−16] even though studies collating results from different experiments[16] reveal in some cases disagreements within the stated uncertainty bars and suggest that the actual accuracy of some high-resolution experimental data sets can be as low as 0.02 cm^{-1}.

However, an accuracy on the part of theory of 0.02 to 0.1 cm^{-1} is sufficient for the unambiguous assignment of experimental spectra. Dense spectra may contain as many as 50 lines per cm^{-1},[17,18] but in such cases, one can usually make use of line intensities to guide the assignment process, so that an accuracy of computed lines of 0.02–0.1 cm^{-1} is adequate for the direct assignment of lines by comparison with calculated spectra.

It therefore seems reasonable to set 0.02–0.1 cm^{-1} accuracy as a goal for theoretical rotational–vibrational line calculations. This accuracy allows virtually the whole range of spectroscopic problems presented by small molecules of which water represents an important benchmark system, to be addressed. In the following, we shall refer to this range as experimental accuracy. Recently, this kind of accuracy was achieved globally for H_3^+,[19] a molecule for which it is a pleasure to note the

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pivotal role played by the distinguished addressee of this special issue.[20−22]

In this article, we will show that it is becoming possible to achieve experimental accuracy from first principles for water and potentially for other molecules of comparable size. For example, it seems very likely that experimental accuracy could be obtained for H_3O^+, another system for which Oka has made major contributions.[23−25]

The gradual improvement in the accuracy of semiempirical water potential energy surfaces (PES)[26−29] has resulted in procedures that can reproduce the observed rotation−vibration energy levels of water with a standard deviation, σ (used synonymously to root-mean-square deviation in this article), close to 0.02 cm^{-1} for a global fit, or even better than this for a restricted set of levels.[30] The use of calculated transition frequencies based on these semiempirical PESs has resulted in the assignment of a large number and range of water spectra (see, for example, refs 31−40). The aim of developing ab initio procedures with an experimental accuracy of about 0.02−0.1 cm^{-1} will allow this methodology to become truly predictive. In this article, we will show that it is becoming possible to achieve this accuracy from first principles.

Attempts to perform accurate calculation of water spectra have a long history, which may be divided into four overlapping stages. The first stage, spanning the period from the 1960s to the mid-1980s, made use of effective Hamiltonians based on perturbation theory (PT). In the standard Watson's form[41] these proved to be slowly convergent and even divergent above certain values of the rotational quantum numbers J and K_a.[42] Various methods were used to sum the divergent PT series.[30,42−44] The second stage, covering the 1980s and 1990s, involved direct solution of the nuclear motion Schrödinger equation expressed in terms of geometrically defined internal coordinates and numerical methods based on the variational principle;[45,46] during this stage, the PES, which in this approach is crucial for the accuracy, was empirically fitted.[47−51] In the third stage, which may be considered to begin with the 1997 paper by Partridge and Schwenke[26] and to be still continuing, it was realized that accurate ab initio surfaces provide a greatly improved starting point for fits to spectroscopic data. Over the last 15 years further improvement in the accuracy of the treatment has been based directly on further improvement in the quality of the ab initio PES[52,53] and non-Born−Oppenheimer (BO) corrections[54−57] used as the starting point of the fit. Improvements in the ab initio surfaces notwithstanding fits of the surfaces to spectroscopic data remain essential for getting results, which approach experimental accuracy. The most recent semiempirical PES[29] gives $\sigma \approx 0.02$ cm^{-1} and demonstrates the state-of-the-art quality achievable by the semiempirical approach. In the fourth stage, the aim is to achieve the same accuracy of empirical and semiempirical approaches entirely from first principles. Achieving this goal would not only show that the behavior of the water molecule is completely understood from a theoretical perspective, but it would also revolutionize the predictive abilities of such calculations.

Recently, some of us accepted the challenge made by Oka and co-workers[22] and showed that near-experimental accuracy of 0.1 cm^{-1} could be achieved for the low-J energy levels of the two-electron H_3^+ molecule up to 17 000 cm^{-1}.[19] Such accuracy was already achieved ab initio some years ago[58] for levels up to 10 000 cm^{-1}, i.e., below the barrier to linearity in H_3^+. Recent developments extended this accuracy to a global PES.[19,59] The source of this accuracy can be ascribed not only to the exceptionally high accuracy of ab initio points[60] but also to the density of the grid of points used (42 000 points were calculated) and to the inclusion of adiabatic, relativistic, and nonadiabatic corrections. This first, purely ab initio result of such quality for a polyatomic molecule provides pointers to how to treat other systems. However, treating polyatomic molecules with more than two electrons to this accuracy is significantly more challenging.[52] In this work, we demonstrate a significant improvement in the accuracy of the ab initio and near-ab initio treatment of the ro-vibrational energy levels of the water molecule.

Currently, the highest-accuracy fully ab initio calculation of ro-vibrational energy levels of water is due to Polyansky et al.[52,53] This work achieved an average accuracy of about 1 cm^{-1} for about 20 000 ro-vibrational energy levels of water up to J = 20 and about 2 cm^{-1} for the water band origins then known, which extended up to 25 000 cm^{-1}. These ab initio calculations were performed using a multireference configuration interaction (MRCI) method using basis sets up to aug-cc-pV6Z and basis set extrapolation. An important part of the calculations was the systematic inclusion of the core−valence, adiabatic, relativistic, and quantum electrodynamic (QED) corrections.[56] Each of these corrections was found to contribute significantly to the improved accuracy. The least significant term was the QED correction, which contributed less than about 1 cm^{-1} to the energy levels and reduced σ by about 0.2 cm^{-1}. The importance of the BODC (Born−Oppenheimer diagonal correction) or adiabatic correction for accurate calculation of ro-vibrational spectra of polyatomic molecules was first shown for H_3^+[61,62] and subsequently for water.[54] Relativistic corrections to the ro-vibrational energy levels are very small for H_3^+[63] but are very important for water[55] and other molecules.[64,65]

Schwenke[57] developed an approximate treatment for the nonadiabatic correction terms, which was considered by Polyansky et al;[52] however, the nonadiabatic contributions was found to be small with respect to the band origin σ = 1.90 cm^{-1} of those calculations. Subsequent work[66−70] investigated further possible improvements in the ab initio calculation of the fundamental frequencies and equilibrium structure of water. These approaches generally employed coupled cluster methods in its F12 manifestation. However, little further improvement in the accuracy of the band origins or excited rotational levels for water was actually achieved.

More recently, we have computed a more sophisticated BO global PES in order to reproduce the experimental values for the water energy levels lying from 27 000 cm^{-1} up to dissociation and above.[71−74] Using the equilibrium energy from this computation augmented by relativistic, QED, adiabatic, and spin−orbit coupling terms reproduces the dissociation energy of both H_2O and HDO experimentally within ±2 cm^{-1}.[75] This unprecedented accuracy suggested that this BO PES[74] could provide a very accurate surface for those geometries close to equilibrium that are important for determining the ro-vibrational energy levels of water up to 15 000 cm^{-1}. The details of our calculations are given below.

■ CALCULATIONS

All nuclear motion calculations reported in this work were performed with the DVR3D program suite[76] and used Radau coordinates. Morse-like basis functions, 25 DVR grid points in each radial coordinate, and 40 angular DVR grid points were

Table 1. Calculated and Observed Energy Levels, in cm^{-1}, for $J = 0$ of $H_2{}^{16}O$[a]

state ($\nu_1\nu_2\nu_3$)	obs	obs − calc				
		adiabatic	+NBO	semi-emp 1	semi-emp 2	semi-emp 3
σ		2.07	0.52	0.23	0.27	0.13
(010)	1594.74	−0.31	−0.22	0.00	−0.02	−0.03
(020)	3151.63	−0.54	−0.40	0.03	0.02	−0.01
(100)	3657.05	−0.84	−0.13	−0.13	0.04	0.03
(030)	4666.78	−0.81	−0.62	0.01	0.02	−0.02
(110)	5234.97	−1.06	−0.22	0.00	0.15	0.13
(040)	6134.01	−1.14	−0.90	−0.09	−0.02	−0.07
(120)	6775.09	−1.37	−0.45	−0.01	0.13	0.10
(200)	7201.54	−1.69	−0.31	−0.31	0.00	−0.02
(002)	7445.04	−1.33	0.14	0.15	0.43	0.19
(050)	7542.43	−1.54	−1.26	−0.29	−0.10	−0.17
(130)	8273.97	−1.71	−0.72	−0.08	0.07	0.04
(210)	8761.58	−1.82	−0.29	−0.06	0.22	0.19
(012)	9000.13	−1.61	−0.06	0.18	0.41	0.16
(220)	10284.36	−2.07	−0.45	−0.01	0.26	0.22
(022)	10521.76	−1.92	−0.32	0.15	0.35	0.07
(300)	10599.68	−2.43	−0.44	−0.43	−0.01	−0.07
(102)	10868.87	−2.37	−0.27	−0.26	0.18	0.06
(230)	11767.38	−2.37	−0.67	−0.02	0.25	0.20
(032)	12007.77	−2.28	−0.62	0.07	0.24	−0.06
(310)	12139.31	−2.51	−0.39	−0.15	0.24	0.17
(112)	12407.66	−2.58	−0.38	−0.13	0.27	0.14
(400)	13828.27	−3.14	−0.63	−0.61	−0.09	−0.17
(122)	13910.89	−2.90	−0.61	−0.15	0.22	0.08
(202)	14221.15	−3.40	−0.77	−0.76	−0.16	−0.24
(004)	14537.50	−2.59	0.20	0.22	0.74	0.26
(001)	3755.92	−0.73	0.03	0.05	0.17	0.04
(011)	5331.26	−0.99	−0.15	0.12	0.19	0.04
(021)	6871.52	−1.23	−0.33	0.19	0.21	0.04
(101)	7249.81	−1.64	−0.20	−0.18	0.09	−0.02
(031)	8373.85	−1.51	−0.54	0.20	0.21	0.01
(111)	8806.99	−1.87	−0.32	−0.05	0.16	0.03
(041)	9833.58	−1.84	−0.82	0.15	0.16	−0.06
(121)	10328.72	−2.14	−0.53	−0.01	0.15	0.01
(201)	10613.35	−2.36	−0.33	−0.31	0.09	−0.01
(003)	11032.40	−1.93	0.24	0.25	0.64	0.27
(051)	11242.77	−2.23	−1.16	0.00	0.07	−0.18
(131)	11813.20	−2.42	−0.76	−0.01	0.13	−0.03
(211)	12151.25	−2.51	−0.37	−0.09	0.24	0.13
(013)	12565.00	−2.24	−0.02	0.26	0.58	0.17
(221)	13652.65	−2.71	−0.49	0.02	0.31	0.18
(301)	13830.93	−3.10	−0.58	−0.53	−0.03	−0.12
(023)	14066.19	−2.61	−0.34	0.18	0.44	0.02
(103)	14318.81	−2.85	−0.10	−0.08	0.45	0.20

[a] Observed levels are taken from Tennyson et al.;[16] calculated levels are given as observed minus calculated (obs − calcd). Column 3, labeled ‘adiabatic’, gives the results relative to the ab initio Born−Oppenheimer surface plus the relativistic, QED, and adiabatic corrections. Column 4, labeled ‘+NBO’ includes ab initio non-Born−Oppenheimer (NBO) corrections and gives our best fully ab initio predictions. Columns 5, 6, and 7, labelled ‘semi-emp 1, 2, and 3’, show the effect of introducing respectively one, two, or three semi-empirical fitting parameters. Semi-emp 1 includes a parameter scaling the non-adiabatic effects, semi-emp 2 includes a further parameter adjusting the angular behavior of the adiabatic PES, and semi-emp 3 further includes a parameter controlling the asymmetric-stretch region of the PES (see text for details). σ is the standard deviation of the obs − calcd.

used. The final matrix size was 1500 for symmetric isotopologues. For HDO calculations were used 30 radial DVR grid points and 48 angular grid points with a final matrix of size 4000. The convergence of energy levels below 15 000 cm^{-1} was better than 0.01 cm^{-1} for all water isotopologues considered.

The main PES used is a new fit of the ab initio calculations presented by Császár et al.[74] and is given in the Supporting Information. Those calculations were performed using MOLPRO[77] at the all-electron, Davidson corrected (+Q) IC-MRCI level, using the aug-cc-pCVnZ (n = Q, 5, and 6) correlation-consistent basis sets.[78−80] All ten electrons were correlated at the MRCI stage, which obviates the need for a separate core−valence correction. The dynamic correlation part of the energies, here defined as the difference between CASSCF and MRCI energies, was extrapolated using the $n = 5$ and $n = 6$ energies and assuming a $E_n = E_\infty + A/n^3$ dependence. CASSCF energies were extrapolated using the n = Q, 5, and 6 values and assuming a $E_n = E_\infty + A\ e^{-\alpha n}$ dependence. The active space used is formed by distributing the eight valence electrons in ten active orbitals (the specification for C_{2v} symmetries is 5 a_1, 3 b_1, and 2 b_2 orbitals) and is larger than the eight-electron, eight-orbital active space used for the CVRQD PES by Barletta et al.[52,81] This level of calculation was originally designed to obtain the high-accuracy LTP2011 dipole moment surfaces for water[82] for which it was found that the enlarged active space gave a substantial improvement. As Császár et a.l[74] did not compute a global adiabatic correction surface, their final PES comprised only the MRCI+Q BO surface plus relativistic correction terms.

Using Császár et al.'s MRCI+Q ab initio points,[74] we constructed a new PES by fitting 1260 points lying at energies less than 25 000 cm^{-1} above the equilibrium value and also excluding 250 points with large energy residuals. By limiting the fit to these points, we were able to obtain an analytic representation of the PES, which reproduces the ab initio points at standard deviation of only 0.3 cm^{-1}, compared to the standard deviation of 2 cm^{-1} produced by the original fit[74] for the global surface. A Fortran program representing this potential along with the 246 fitting parameters is given in the Supporting Information.

This surface was augmented with a relativistic correction, a QED correction, and an adiabatic correction; the relativistic correction was also computed by Császár et al.[73] and is based on the expectation value of the mass-velocity plus one-electron Darwin operator (MVD1) computed with the MRCI/aug-cc-pCV6Z wave function. Our approximate QED correction is very simply given by 0.0238 times the one-electron Darwin term.[56] Finally, the adiabatic correction surface was taken from the CVRQD PES.[52,53]

This surface was used initially to calculate the $J = 0$ energy levels, hereafter referred to as band origins, for the main water isotopologue $H_2{}^{16}O$ up to 15 000 cm^{-1}. Differences between observed and calculated (obs − calc) energy levels are reported in the column 'adiabatic' of Table 1 corresponding to the PES obtained as the sum of the main Born−Oppenheimer PES and of relativistic, QED, and adiabatic corrections. Results for the $H_2{}^{16}O$ isotopologue are also represented graphically in Figure 1. As one can see the (obs−calc) values are mostly in the range 1 to 2.5 cm^{-1} and, very importantly, proportional to known shifts in the energy levels produced by inclusion of the vibrational nonadiabatic contributions as first calculated by Schwenke.[57]

The next step was therefore the inclusion of nonadiabatic corrections based on the vibrationally averaged constants given by Schwenke.[57] The calculations of nonadiabatic coupling curves involves in this approach matrix elements of various nonadiabatic coupling operators between the ground electronic state and excited electronic states. Schwenke[57] computed these coupling terms using the Hartree−Fock wave function for the ground state and single-excitation configuration interaction for the excited states. Schwenke showed that, in the case of the H_2 molecule, his approximate model recovered 80% to 90% of the exact nonadiabatic effects, which for H_2 have been computed independently and very accurately many times;[83−85] he also demonstrated that the accurate nonadiabatic shifts in H_2 could be reproduced to 0.01 cm^{-1} by simply scaling the nonadiabatic constants of his model by the factor 1.14. He suggested an analogous scaling of the nonadiabatic constants for water by the factor 1.1 on the basis of comparison with experimental rotational g factors. Such scaling did not actually improve the (obs − calc) values of his water energy level calculations, in agreement with our earlier calculations,[52] since the main Born−Oppenheimer PESs used in those studies were not accurate enough.

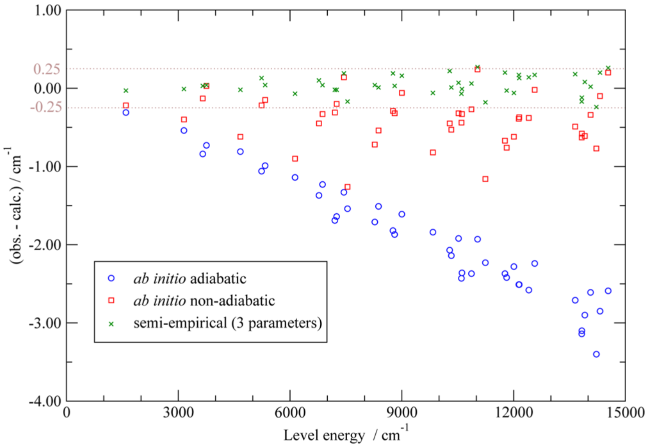

Figure 1. Plot of residuals (obs − calc) for $J = 0$ energy levels for H_2O. The data set represented in this figure correspond to the third, fourth, and last column of Table 1. The dotted lines correspond to a range of ±0.25 cm^{-1}, which is the maximum deviation of our semiempirical, 3-parameter fit.

In this work, we adopt the model introduced by Schwenke[57] in its simplified version, namely, assuming all correction functions to be constants and neglecting terms involving cross-derivatives. In this model, nonadiabatic corrections to vibrations are controlled by two constants (one affecting mainly stretches and one mainly bends), while three further constants affect nonadiabatic effects to rotations. In the case of $J = 0$ energy levels, we adjusted the two nonadiabatic parameters and the final results of our tests are given in Tables 1−5 for the five major water isotopologues. The standard deviation (σ) of a calculation using our Born−Oppenheimer PES with relativistic, QED, and adiabatic corrections is about 1.5 cm^{-1}. The fourth column of the tables gives the (obs − calc) for purely ab initio calculations with the vibrational nonadiabatic constants fixed to the values computed by Schwenke.[57] Adding nonadiabatic corrections improves very significantly the calculations and gives $\sigma \approx 0.3$−0.4 cm^{-1}. This is our best purely ab initio result.

Adjusting the nonadiabatic parameters has been found to be necessary in all the semiempirical fits that used them.[27−29] These adjustments probably reflect the limited accuracy of the procedure used to determine nonadiabatic corrections.[57] Column 5 of Tables 1−5, labeled 'semi-emp 1', presents results obtained by setting the factor multiplying the angular nonadiabatic term[57] to 4.5. Use of only one scaled parameter reduces σ by a factor of 2.

However, comparisons between calculations for different isotopologues suggest that there is a residual source of error in the mass-independent contribution. The most apparent problem is the relatively large deviation of computed energy levels for highly excited bending states. Energies for highly excited bending states of $H_2{}^{16}O$ were determined experimentally in a series of studies,[86−88] which identified monodromy

Table 2. Calculated and Observed Energy Levels, in cm^{-1}, for $J = 0$ of $H_2{}^{18}O$; Observed Levels Are Taken from Tennyson et al.;[14,15] See Footnote *a* of Table 1 for Details of the Column Headings

state ($\nu_1\nu_2\nu_3$)	obs	obs − calc				
		adiabatic	+NBO	semi-emp 1	semi-emp 2	semi-emp 3
σ		1.93	0.35	0.23	0.26	0.13
(010)	1588.28	−0.25	−0.19	0.02	0.01	0.00
(020)	3139.05	−0.50	−0.37	0.05	0.04	0.01
(100)	3649.69	−0.84	−0.05	−0.12	0.04	0.04
(030)	4648.48	−0.77	−0.58	0.03	0.04	0.00
(110)	5221.24	−0.98	−0.13	0.01	0.16	0.14
(040)	6110.42	−1.12	−0.87	−0.09	−0.02	−0.07
(120)	6755.51	−1.26	−0.35	0.01	0.14	0.12
(200)	7185.88	−1.70	−0.17	−0.30	0.01	−0.02
(002)	7418.72	−1.31	0.30	0.16	0.43	0.21
(130)	8249.04	−1.58	−0.61	−0.06	0.09	0.05
(210)	8739.53	−1.71	−0.13	−0.04	0.24	0.20
(012)	8967.57	−1.54	0.12	0.22	0.45	0.20
(220)	10256.58	−1.91	−0.27	0.02	0.29	0.24
(022)	10483.22	−1.90	−0.17	0.14	0.34	0.06
(300)	10573.92	−2.41	−0.22	−0.41	0.01	−0.06
(102)	10839.96	−2.36	−0.06	−0.26	0.19	0.07
(230)	11734.53	−2.20	−0.50	0.00	0.26	0.21
(032)	11963.54	−2.23	−0.44	0.09	0.27	−0.03
(310)	12106.98	−2.40	−0.17	−0.13	0.25	0.17
(112)	12372.71	−2.49	−0.14	−0.11	0.29	0.16
(202)	14187.98	−3.45	−0.49	−0.75	−0.16	−0.23
(001)	3741.57	−0.71	0.11	0.06	0.18	0.06
(011)	5310.46	−0.93	−0.04	0.15	0.22	0.07
(021)	6844.60	−1.18	−0.22	0.21	0.24	0.06
(101)	7228.88	−1.58	−0.05	−0.17	0.11	−0.01
(031)	8341.11	−1.47	−0.44	0.22	0.23	0.03
(111)	8779.72	−1.75	−0.16	−0.02	0.19	0.06
(041)	9795.33	−1.81	−0.71	0.16	0.18	−0.05
(121)	10295.63	−2.02	−0.36	0.01	0.18	0.03
(201)	10585.29	−2.34	−0.15	−0.32	0.08	−0.02
(003)	10993.68	−1.90	0.45	0.26	0.65	0.28
(131)	11774.71	−2.32	−0.58	0.01	0.15	−0.01
(211)	12116.80	−2.41	−0.17	−0.09	0.24	0.13
(113)	12520.12	−2.18	0.22	0.28	0.61	0.21
(221)	13612.71	−2.61	−0.30	0.02	0.30	0.17
(301)	13795.40	−3.18	−0.42	−0.64	−0.13	−0.22
(103)	14276.34	−2.83	0.14	−0.10	0.44	0.19

behavior[89] in the energy levels of water for the first time.[88] Given that the height of the barrier to linearity (the monodromy point) is the hardest feature to determine accurately for water, we already had to address the problem of anomalously large discrepancies for excited bending energy levels compared to stretching ones.[90] This is because the barrier height is much more sensitive to basis set convergence than the stretching part of the potential.[52] Our previous study showed that the introduction of a simple, two-term, one-dimensional phenomenological curve to the PES helped in reducing σ for the ab initio Partridge and Schwenke (PS) PES[26] from about 10 to 2 cm^{-1}; this correction curve gave a significant change in the angular behavior and much smaller differences for the radial components.

PS used an aug-cc-pV5Z basis set (with extrapolation), and the bending states change significantly on use of extrapolation for an aug-cc-pV6Z basis set.[52] To improve the situation further, one should employ a basis of at least 7Z quality. However, such basis sets are not fully usable in MOLPRO, or indeed other equivalent quantum chemistry programs available to us, since they require the computation of integrals involving k ($l = 7$) angular functions. This situation is clearly analogous to that encountered before,[90] although the required correction should be much smaller. Thus to model the hypothetical effect of aug-cc-pV7Z (or higher) functions, we introduced the barrier term of Kain et a.l[90] sharply scaled down by a factor of 0.06. Use of this extra term significantly improves the behavior of the bending energy levels for $\nu_2 > 5$. Tellingly, by including the extra term, the optimal scaling parameters for the nonadiabatic terms becomes much closer to their ab initio values. Whereas in the column 5 the results were obtained with an unrealistically large scaling factor, 4.5, the results presented in column 6, which include the one-dimensional barrier to linearity, were obtained by scaling *both* nonadiabatic constants by only 1.25. Such value is fully consistent with the observation by Schwenke[57] that his calculation procedure is only about 80% accurate. We should stress that the results of column 6 are obtained using two parameters only: one scaling the non-

Table 3. Calculated and Observed Energy Levels, in cm^{-1}, for $J = 0$ of $D_2{}^{16}O$; Observed Levels Are Taken From ref 91 Where References to All Original Observations Are Given; See Footnote *a* of Table 1 for Details of the Column Headings

state ($v_1v_2v_3$)	obs	obs − calc				
		adiabatic	+NBO	semi-emp 1	semi-emp 2	semi-emp 3
σ		0.88	0.23	0.13	0.14	0.08
(010)	1178.38	−0.32	−0.28	−0.12	−0.13	−0.14
(020)	2336.84	−0.49	−0.40	−0.09	−0.10	−0.12
(100)	2671.65	−0.26	0.00	0.01	0.07	0.06
(030)	3474.32	−0.60	−0.46	0.00	−0.01	−0.04
(120)	4990.83	−0.62	−0.26	0.05	0.09	0.07
(200)	5291.72	−0.59	−0.07	−0.07	0.05	0.03
(002)	5529.44	−0.41	0.15	0.15	0.21	0.03
(210)	6452.98	−0.69	−0.13	0.04	0.14	0.12
(012)	6686.99	−0.67	−0.07	0.10	0.13	−0.06
(300)	7852.93	−0.96	−0.20	−0.19	−0.03	−0.06
(112)	9202.72	−0.95	−0.12	0.06	0.15	−0.02
(410)	11483.64	−1.26	−0.25	−0.05	0.11	0.05
(212)	11679.39	−1.24	−0.19	0.00	0.16	0.05
(001)	2787.72	−0.25	0.04	0.04	0.07	−0.02
(011)	3956.01	−0.53	−0.20	−0.01	−0.02	−0.12
(021)	5105.39	−0.69	−0.31	0.05	0.02	−0.10
(101)	5373.90	−0.60	−0.07	−0.06	0.02	−0.08
(031)	6235.08	−0.81	−0.38	0.15	0.10	−0.04
(111)	6533.24	−0.79	−0.21	−0.02	0.02	−0.09
(201)	7899.83	−0.92	−0.15	−0.14	−0.01	−0.10
(003)	8220.18	−0.55	0.26	0.27	0.36	0.07
(211)	9050.35	−1.03	−0.22	−0.02	0.07	−0.03
(013)	9366.31	−0.81	0.05	0.24	0.28	−0.02
(221)	10180.12	−1.15	−0.29	0.08	0.14	0.03
(301)	10358.56	−1.19	−0.21	−0.19	−0.02	−0.11
(311)	11500.25	−1.25	−0.23	−0.01	0.11	0.02
(113)	11816.64	−1.11	−0.04	0.17	0.26	0.02
(321)	12618.91	−1.31	−0.24	0.13	0.23	0.13
(401)	12743.02	−1.51	−0.33	−0.29	−0.09	−0.18

adiabatic constants given by Schwenke and the other one adjusting the correction to the barrier to linearity given by Kain et al. These two parameters improve σ to 0.2 cm^{-1} but leave (obs − calc) at about 0.4 cm^{-1} for the asymmetric stretches, which are significantly larger than the corresponding discrepancy for the other levels. We therefore introduced one more phenomenological parameter with a functional form suitable for the asymmetric radial part of the PES. The whole adiabatic PES was multiplied by a correction factor R given by

$$R = 1 + \varepsilon(r_1 - r_2)\, \mathrm{e}^{-\beta(r_1+r_2-2r_e)^4}$$

where r_1 and r_2 are bond lengths, $\varepsilon = 0.00012$, $r_e = 1.81a_0$, and $\beta = 2$.

Therefore, altogether we introduced two phenomenologically determined correction curves for the ab initio PES and one nonadiabatic scaling parameter. So the results of column 7 are obtained with these 3 adjusted parameters altogether. With these adjustments, about 200 band origins belonging to 7 water isotopologues can be calculated with an accuracy $\sigma = 0.08$ cm^{-1}. Data for the 5 major water isotopologues are presented in Tables 1−5; the residuals for the main isotopologue $H_2{}^{16}O$ are also illustrated in Figure 1, which shows that, for our final model, practically all residuals are within the ±0.25 cm^{-1} lines.

The levels considered only extend up to 15 000 cm^{-1}, as treating higher energy levels would require the introduction of coordinate dependence in the factors multiplying the derivative operators in the nonadiabatic terms; see formula (55) of Schwenke.[57]

Clearly $J = 0$ calculations are important for testing the quality of a PES and associated model, but excited rotational calculations are also necessary to show that we can compute the energy levels, and indeed the frequencies of water line centers, with an accuracy approaching that of experiment with almost purely ab initio methods. Moreover, as shown elsewhere,[94] a PES that gives excellent results for the vibrations may still be very poor for ro-vibrational levels. Thus, a test of our calculations for excited J values is necessary.

To calculate excited ro-vibrational states, we used the rotational nonadiabatic constants calculated by Schwenke.[57] The use of Schwenke's B and C constants, responsible for the magnitude of the J_x and J_y terms, respectively, without any modifications resulted in very accurate values of the rotational energy levels for low K_a (Table 6). However, to calculate high K_a levels with the same accuracy, we had to adjust Schwenke's nonadiabatic A constant by multiplying it by the factor minus 0.6. This value, unlike the small scale factors of about 1.25 used for vibrational nonadiabatic terms, which could be justified by imperfections in their ab initio determination, is rather significant (Table 6). At present, we do not have a theoretical explanation of the reason why this constant changes sign; however, we point to a similar value for this adjustment factor, including the sign change, obtained by Shirin et al.,[27] while obtaining a high quality semiempirical PES. It would therefore

Table 4. Calculated and Observed Energy Levels, in cm^{-1}, for $J = 0$ of HD^{16}O; Observed Levels Are Taken from Tennyson et al.;[15] See Footnote *a* of Table 1 for Details of the Column Headings

		obs − calc				
state ($v_1v_2v_3$)	obs	adiabatic	+NBO	semi-emp 1	semi-emp 2	semi-emp 3
σ		1.56	0.30	0.24	0.09	0.08
(010)	1403.48	−0.31	−0.09	−0.06	−0.07	−0.07
(100)	2723.68	−0.25	−0.02	0.02	0.06	0.04
(020)	2782.01	−0.46	−0.03	0.02	0.00	0.00
(001)	3707.47	−0.83	−0.19	−0.18	−0.05	−0.02
(110)	4099.96	−0.61	−0.04	0.01	0.02	0.02
(030)	4145.47	−0.52	0.03	0.09	0.10	0.08
(011)	5089.54	−1.05	−0.19	−0.15	−0.05	−0.02
(200)	5363.82	−0.54	−0.11	−0.03	0.05	0.02
(040)	5420.04	−0.85	0.03	0.07	0.08	0.09
(101)	6415.46	−1.03	−0.13	−0.08	0.08	0.09
(021)	6451.90	−1.20	−0.17	−0.11	0.00	0.03
(050)	6690.41	−1.20	−0.05	−0.07	0.00	0.02
(210)	6746.91	−0.73	−0.05	0.06	0.11	0.08
(002)	7250.52	−1.63	−0.40	−0.38	−0.13	−0.09
(031)	7754.61	−1.39	−0.15	−0.08	0.02	0.06
(111)	7808.76	−1.27	−0.14	−0.06	0.07	0.08
(060)	7914.32	−1.58	−0.18	−0.30	−0.11	−0.10
(300)	7918.17	−0.84	−0.17	−0.08	0.04	0.01
(012)	8611.10	−1.78	−0.35	−0.29	−0.08	−0.03
(201)	9047.07	−1.37	−0.21	−0.17	0.06	0.05
(121)	9155.82	−1.48	−0.18	−0.08	0.06	0.06
(310)	9293.00	−0.94	−0.07	0.07	0.15	0.12
(150)	9381.79	−1.38	−0.09	−0.01	0.07	0.05
(230)	9487.92	−1.23	−0.10	0.03	0.11	0.06
(102)	9967.02	−1.85	−0.35	−0.28	−0.02	0.01
(400)	10378.95	−1.15	−0.20	−0.09	0.06	0.04
(003)	10631.68	−2.26	−0.56	−0.48	−0.14	−0.11
(032)	11242.92	−2.10	−0.28	−0.17	0.01	0.07
(112)	11315.43	−1.95	−0.28	−0.18	0.07	0.09
(221)	11701.78	−1.86	−0.25	−0.14	0.03	0.03
(410)	11754.58	−1.47	−0.18	−0.08	0.09	0.06
(170)	11773.31	−1.82	−0.24	−0.24	0.00	−0.02
(013)	11969.75	−2.40	−0.50	−0.38	−0.07	−0.05
(500)	12767.14	−1.30	−0.28	−0.17	0.01	0.01
(023)	13278.36	−2.53	−0.45	−0.30	−0.02	0.01
(103)	13331.61	−2.50	−0.55	−0.45	−0.06	−0.04
(004)	13853.63	−2.98	−0.88	−0.73	−0.30	−0.31
(510)	14147.43	−1.58	−0.26	−0.10	0.07	0.06
(113)	14660.72	−2.61	−0.47	−0.12	0.03	0.04
(600)	15065.71	−1.77	−0.56	−0.45	−0.25	−0.23

Table 5. Calculated and Observed Energy Levels, in cm^{-1}, for $J = 0$ of T$_2$^{16}O; Observed Levels Are Taken From ref 54 Based Earlier Experiments;[92,93] See Footnote *a* of Table 1 for Details of the Column Headings

		obs − calc				
state ($v_1v_2v_3$)	obs	adiabatic	+NBO	semi-emp 1	semi-emp 2	semi-emp 3
σ		0.19	0.14	0.08	0.10	0.10
(010)	995.37	−0.27	−0.23	−0.10	−0.11	−0.12
(100)	2237.15	−0.07	0.08	0.08	0.12	0.11
(001)	2366.61	−0.16	0.02	0.03	0.03	−0.07

appear that there is a problem with this rotational nonadiabatic term and not our particular calculation.

The overall σ for the $J = 20$ levels with this adjustment is 0.14 cm^{-1}, and calculation of all known energy levels up to $J = 20$ resulted in $\sigma \approx 0.12$ cm^{-1}. We have checked σ for different J levels in the present model and for the most accurate semiempirical PES due to Bubukina et al.[29] For low J, Bubukina et al.'s σ is about 0.03 cm^{-1}, which is a few times better than our present model for which σ is practically independent of J and about 0.14 cm^{-1} for all J. However, with increasing J, the accuracy of Bubukina et al.'s model deteriorates and, at about $J = 20$, became equal to ours. For levels with $J > 20$, our near ab

Table 6. Calculated and Observed Term Values, in cm^{-1}, for J = 20 of the Ground (000) Vibrational State of $H_2{}^{16}O$; Observed Levels Are Taken from Tennyson et al.[16a]

		obs − calc	
state (J, K_a, K_c)	obs	A	B
σ		1.06	0.10
20 0 20	4048.25	0.13	0.09
20 1 20	4048.25	0.13	0.09
20 1 19	4412.32	0.14	0.05
20 2 19	4412.32	0.14	0.05
20 2 18	4738.62	0.15	0.01
20 3 18	4738.63	0.15	0.01
20 3 17	5031.79	0.16	−0.03
20 4 17	5031.98	0.16	−0.03
20 4 16	5292.10	0.15	−0.07
20 5 16	5294.04	0.16	−0.06
20 5 15	5513.24	0.11	−0.10
20 6 15	5527.05	0.15	−0.09
20 6 14	5680.79	0.03	−0.15
20 7 14	5739.23	0.17	−0.12
20 7 13	5812.07	0.03	−0.17
20 8 13	5947.31	0.23	−0.12
20 8 12	5966.82	0.16	−0.15
20 9 12	6167.72	0.33	−0.12
20 9 11	6170.83	0.31	−0.14
20 10 11	6407.08	0.44	−0.13
20 10 10	6407.44	0.44	−0.13
20 11 10	6664.14	0.57	−0.13
20 11 9	6664.17	0.57	−0.13
20 12 9	6935.43	0.71	−0.12
20 12 8	6935.43	0.71	−0.12
20 13 8	7217.56	0.85	−0.13
20 13 7	7217.56	0.85	−0.13
20 14 7	7507.54	0.99	−0.15
20 14 6	7507.54	0.99	−0.15
20 15 6	7802.71	1.21	−0.10
20 15 5	7802.71	1.21	−0.10
20 16 5	8100.29	1.41	−0.09
20 16 4	8100.29	1.41	−0.09
20 17 4	8397.65	1.63	−0.06
20 17 3	8397.65	1.63	−0.06
20 18 3	8691.93	1.87	−0.03
20 18 2	8691.93	1.87	−0.03
20 19 2	8979.88	2.14	0.00
20 19 1	8979.88	2.14	0.00
20 20 1	9257.46	2.44	0.05
20 20 0	9257.46	2.44	0.05

[a] Results in the column labelled A refer to calculations perfomed using the adiabatic PES, three scaled vibrational non-adiabatic constants, and ab initio (i.e., unadjusted) rotational non-adiabatic constants taken from ref 57. Results in column B additionaly scale one of the ab initio rotational non-adiabatic constants by the factor −0.60 (see text).

initio calculations are more accurate. This is an important result. It shows, that even now without further improvements, we can predict line centers for transitions involving rotational quantum states with J higher than 20 with an accuracy better than that of the best semiempirically or spectroscopically determined PES.[29] Note that 246 parameters were adjusted in this semiempirical fit.

DISCUSSION

As the water molecule serves as a benchmark system for studies of similar molecules, we consider in this section the implications of our findings for the calculation of rotation−vibration spectra of other small molecules from first principles. The results presented here could be developed in a number of directions.

First, the two empirical curves correcting the adiabatic PES could in principle be obtained ab initio. Doing this requires better convergence with respect to the basis set used. One possibility is to repeat the calculation using the aug-cc-pV7Z or even the aug-cc-pV8Z basis sets; these basis sets are already available for water[70] but, as discussed above, not fully usable with current software at the MRCI level. Another possibility is to exploit the better basis set convergence of F12 methods, which have recently become available at the MRCI level.[95] However, at the moment, the necessary basis sets for using F12 methods in high-accuracy work (e.g., large basis sets for the resolution-of-identity approximation and for core−valence correlation) are not available, and this fact strongly limits the actual accuracy achievable in practice with this promising approach.[96]

Second, if one compares the results of Schwenke's Table 5[57] with those of Table 1 above, one can see that the differences between Schwenke's more complete nonadiabatic treatment and its simplified version (used in this work) are often similar to the final (obs − calc) column in Tables 1−5. This implies that a more complete inclusion of the nonadiabatic corrections should further improve our results.

Third, all-electron aug-cc-pV6Z calculations for molecules such as HCN, H_2S, and CO_2, which have more electrons, are now computationally feasible. PES calculations are currently possible at this level for molecules with up to 20 to 25 electrons. This means that ab initio calculations on other triatomic molecules of interest should be possible, which, once all the minor corrections have been included, should give similar close-to-experimental accuracy.

Fourth, calculations of aug-cc-pV6Z level BO surfaces of tetra- and penta-atomic molecules, which are electronically similar to water, can be computed, hopefully with a similar level of accuracy. Examples include NH_3, H_3O^+, and CH_4. As H_3O^+ is a ten-electron system like water, we might legitimately expect that theoretical procedures, which are robust for water can be directly transferred to H_3O^+. We hope to be able to calculate the energy levels of this molecular ion, which is extremely important in the theory of liquid water, to the same level of accuracy as we do for water in this article. Such work would also facilitate experimental observation of H_3O^+ lines up to dissociation.

Finally, this article concentrates solely on the calculation of accurate rotation−vibration energy levels and associated wave functions. However, spectral lines also have an intensity and theory can be particularly accurate in calculating line intensities, which are often hard to measure accurately.[97] We note that the developments of ab initio methods, which we exploit here, have also been used to compute very high accuracy dipole moment surfaces (DMS) for water.[82] This DMS has been shown to give excellent predictions,[98,99] and intensities computed with it are beginning to supersede measurements as the reliable source of spectroscopic data for water isotopologues.[100] The biggest residual problem in this approach is not the accuracy of the DMS itself but our ability to compute accurately rotation−

vibration wave functions.[98,100] Clearly, the ab initio approach outlined here could provide a major advance in addressing this problem.

■ CONCLUSIONS

We present results of ab initio calculations for the vibrational and ro-vibrational energy levels of the water molecule and its isotopologues performed at an unprecedented level of accuracy. For the 200 or so known rotationless, $J = 0$ levels of water, which lie below 15 000 cm^{-1}, our purely ab initio accuracy is 0.3 cm^{-1}. Use of three scaling parameters, to correct (largely) known defects in the ab initio procedure, reduces this standard deviation to 0.08 cm^{-1}. Excited rotational levels are calculated ab initio with an accuracy of about 0.1 cm^{-1}. For levels above $J = 20$, our ab initio accuracy actually improves on that given by the best-available, global semiempirical model.[29] This major improvement came from the fact that very accurate BO PESs were used in conjunction with the non-BO corrections. In particular, nonadiabatic corrections were used in the kinetic energy operators with a form that goes beyond simple mass-scaling.[58] The accuracy achieved here is only about a factor of 5 away from the near-experimental accuracy of about 0.02 cm^{-1} that can be obtained using a completely semiempirical approach.[29] Results at this level were only possible for two-electron systems such H_3^+ and H_2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

We provide as a Fortran subroutine the main, nonrelativistic Born−Oppenheimer potential energy surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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