

CVRQD *ab initio* ground-state adiabatic potential energy surfaces for the water molecule

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The high accuracy *ab initio* adiabatic potential energy surfaces (PESs) of the ground electronic state of the water molecule, determined originally by Polyansky *et al.* [Science **299**, 539 (2003)] and called CVRQD, are extended and carefully characterized and analyzed. The CVRQD potential energy surfaces are obtained from extrapolation to the complete basis set of nearly full configuration interaction valence-only electronic structure computations, augmented by core, relativistic, quantum electrodynamics, and diagonal Born-Oppenheimer corrections. We also report *ab initio* calculations of several quantities characterizing the CVRQD PESs, including equilibrium and vibrationally averaged (0 K) structures, harmonic and anharmonic force fields, harmonic vibrational frequencies, vibrational fundamentals, and zero-point energies. They can be considered as the best *ab initio* estimates of these quantities available today. Results of first-principles computations on the rovibrational energy levels of several isotopologues of the water molecule are also presented, based on the CVRQD PESs and the use of variational nuclear motion calculations employing an exact kinetic energy operator given in orthogonal internal coordinates. The variational nuclear motion calculations also include a simplified treatment of nonadiabatic effects. This sophisticated procedure to compute rovibrational energy levels reproduces all the known rovibrational levels of the water isotopologues considered, H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, and D₂¹⁶O, to better than 1 cm⁻¹ on average. Finally, prospects for further improvement of the ground-state adiabatic *ab initio* PESs of water are discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2378766]

I. INTRODUCTION

The water molecule is very important in its own right as the most significant absorber of sunlight in the Earth's atmosphere and, consequently, as the major greenhouse gas. It is the third most common molecule, after H₂ and CO, in the universe, and thus its spectroscopy has considerable astrochemical and astrophysical implications. Nearly all spectroscopic properties of free water can be characterized by tran-

sitions between vibration-rotation energy levels of its electronic ground state. As a ten-electron, closed shell, triatomic system the spectroscopic properties of the electronic ground state of water are complicated enough not to be precisely soluble but simple enough for high accuracy computational solutions to be attempted. The rovibrational spectrum of water has therefore served for some time as a benchmark against which various quantum mechanical procedures have been assessed.¹⁻¹¹

The canonical process of obtaining accurate computational predictions for the rotational-vibrational spectrum of single molecules is normally divided into two steps. First, one or more potential energy surfaces (PESs), and possibly

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property surfaces [such as the dipole moment surface (DMS)] are obtained, based on solving the electronic part of the Schrödinger equation on a grid including a large number of nuclear structures. Second, the PESs, usually after proper fitting, are used to solve the nuclear motion problem, while the appropriate property surfaces are then used to obtain the full spectrum.

In both steps, there are several factors which affect the accuracy of a first-principles computation of rovibrational spectra. Calculations based on variational procedures for the triatomic nuclear motion problem far from dissociation can be made effectively exact within the Born-Oppenheimer approximation.¹⁰ Therefore, comparison of quantum chemical computations based on the use of variational procedures^{1,3,4,9} reduces to comparisons between solutions of the electronic structure problem plus any possible allowance for the failure of the Born-Oppenheimer separation of electronic and nuclear motions. Therefore, in an accurate prediction of the complete rovibrational spectrum of water it is the computation of the PES which needs to be improved. We recently briefly reported results of a study aimed at obtaining an accurate as possible solution to the water vibration-rotation problem below $25\,000\text{ cm}^{-1}$,⁴ which more or less corresponds to the limit of experimentally observed transitions. This study combined electronic structure calculations pushed to the technical limits with a detailed consideration of effects routinely neglected in more approximate studies. Our work resulted in a highly accurate PES denoted CVRQD,¹¹ where the abbreviation stands for a composite surface including core, valence, relativistic, quantum electrodynamics, and diagonal Born-Oppenheimer correction surfaces, and it reproduced the known experimental rovibrational energy levels of several of the isotopologues of water to better than 1 cm^{-1} on average. While this cannot be said to constitute true spectroscopic accuracy, it met the criterion set forth by electronic structure theorists and it is nearly an order of magnitude better than the previous best attempt to solve the same problem.³

Since the original publication⁴ of the CVRQD PESs lacked sufficient detail about the concerns leading to and the procedures resulting in the surfaces, as well as a detailed discussion of the energy points and surfaces, the principal intent of this paper is to fill this gap. Furthermore, this study provides not only an analysis of the *ab initio* surfaces of water but also the prospects for further improvement of the ground-state adiabatic *ab initio* PESs of water. The surfaces presented in this paper and the previously unpublished underlying energy points are given in the electronic archive¹² to facilitate their use by other workers interested in the spectroscopy of water.

II. ELECTRONIC STRUCTURE CALCULATIONS

The *ab initio* adiabatic electronic ground-state CVRQD PESs of the water isotopologues considered were constructed from several parts, as follows: (a) the final PES is built upon valence-only augmented correlation-consistent aug-cc-pVnZ,^{13,14} $n=4, 5$, and 6 , internally contracted multireference configuration interaction¹⁵ (ICMRCI) calculations

including the size-extensivity Davidson correction (+ Q),¹⁶ performed with the electronic structure package MOLPRO,¹⁷ which were extrapolated to the complete basis set (CBS) limit at each grid point; added to this there are several corrective surfaces including (b) the core correlation surface of Partridge and Schwenke,³ determined at a different set of points at the averaged coupled pair functional¹⁸ (ACPF) level employing a quadruple-zeta basis set and the program MOLPRO;¹⁷ (c) the relativistic surface obtained by first-order perturbation theory as applied to the one-electron mass-velocity (MV) and one- and two-electron Darwin terms (MVD2),^{19,20} calculated using the program packages ACESII (Ref. 21) and DALTON,²² supplemented by a correction obtained from the inclusion of the Breit term in the electronic Hamiltonian²⁰ calculated using four-component Dirac-Hartree-Fock wave functions utilizing the program package BERTHA;²³ (d) the correction surface due to effects from quantum electrodynamics (QED) represented by the one-electron Lamb shift;²⁴ and (e) finally, the Born-Oppenheimer adiabatic correction surface obtained at the cc-pVTZ MRCI level.⁴ Each of these surfaces is discussed below separately in varying detail.

Supplementary electronic structure calculations have also been performed during the course of this work, as detailed in the tables of this paper. Computations for the valence-only full configuration interaction (FCI) energies and core correlation corrections were performed with the help of the MRCC (Refs. 25 and 26) and ACESII (Ref. 21) packages, in case employing an approximate treatment of triple excitations at the coupled cluster level, CCSD(T).²⁷ The MRCI and MR-AQCC (Ref. 36) calculations were done with the program COLUMBUS.²⁸ The diagonal Born-Oppenheimer correction (DBOC) calculations²⁹ utilized the PS3 (Ref. 30) package.

Because of an often favorable error compensation between the incompleteness of the basis set and deficiencies in the treatment of electron correlation, as well as the use of approximate Hamiltonians, lower-level electronic structure computations often result in surprisingly small errors for a particular property. This useful practical approach is not pursued here as, instead, this study focuses on the convergence of electronic structure theory to obtain the best technically possible adiabatic PESs for the major isotopologues of water.

In order to explore the convergence of the electronic energies over the whole range of interest of the nuclear coordinates, we have selected ten reference nuclear structures. They are shown in Table I. Structure 1 corresponds approximately to the equilibrium structures of the CVRQD PESs, whereas the others are varied and include symmetrically and asymmetrically stretched, bent, as well as almost linear configurations.

A. Valence-only energies

Within the Born-Oppenheimer approximation and using a finite basis set, an exact solution to the electronic motion problem is offered by the variational and size-consistent (FCI) technique.^{31–33} However, the use of FCI for many-electron systems is only feasible with small basis sets. These

TABLE I. Selected reference structures for the characterization of the CVRQD PESs of water. r_1 and r_2 are the O–H₁ and O–H₂ distances in angstroms, and θ is the H–O–H angle in degrees.

No.	r_1	r_2	θ	No.	r_1	r_2	θ
1	0.9576	0.9576	104.52	6	0.9500	0.9500	170.00
2	0.9000	0.9000	104.52	7	0.9500	0.9500	45.00
3	1.2500	1.2500	104.52	8	0.9500	1.2500	179.90
4	0.7500	0.7500	100.00	9	0.8500	1.3500	104.52
5	1.4000	1.4000	100.00	10	0.9500	2.0000	104.52

computations are, of course, inappropriate in themselves to yield highly accurate PESs. Very accurate approximations to FCI have been developed.^{15,25,31–36} The one used in this study is called MRCI. The underlying complete active space self-consistent field (CASSCF) computations were performed with the same active space as advocated by Partridge and Schwenke,³ six a' and two a'' orbitals (in C_s symmetry) and eight electrons were active. This technique is still variational but lacks size consistency, which was corrected using the Davidson correction. To make calculations with very large basis sets feasible with this technique, the internally contracted (IC) version¹⁵ of the MRCI approach was used.

Dunning¹³ has developed a series of so-called correlation consistent (cc) Gaussian basis sets, (aug-)cc-pVnZ, which approach completeness systematically, allowing for reliable extrapolation. In this notation n stands for the highest angular momentum function in the basis set used and aug specifies that the basis is augmented with diffuse, i.e., low-exponent Gaussian functions. As n increases, the basis set approaches completeness, both by increasing the flexibility for a given symmetry and by including higher angular momentum components. The biggest basis we consider has $n = 6$, and consists of $s, p, d, f, g, h,$ and i functions for oxygen and $s, p, d, f, g,$ and h functions for hydrogen. We found full augmentation of the basis with diffuse functions (aug) to be of particular importance (see below). As required by these (aug-)cc-pVnZ basis sets, the oxygen $1s$ core electrons were kept frozen during the valence-only calculations.

Even though the aug-cc-pV6Z Gaussian basis set contains functions with orbital angular momentum up to i for O, it is still not large enough to fully converge the valence CI

problem. The slow convergence with respect to n is due mostly to the fact that the form of the electronic wave function employed does not describe effectively the region where the two electrons approach each other (Coulomb hole).^{37,38} The related cusp condition requires a prescribed behavior when the distance between two electrons approaches zero, which is approximated with extreme difficulty by the present computations.

In Table II we report relative energies from a series of valence-only electronic structure computations using cc basis sets¹⁴ with $n=2$ (or D), 4 (or Q), 5, and 6 at the ten reference structures of Table I, employing MRCI, ICMRCI, and FCI treatments. In Table II, the basis sets denoted nZ correspond to aug-cc-pVnZ. The relatively large changes in the absolute energies, on the order of hundreds of cm^{-1} , even in the series $5Z \rightarrow 6Z \rightarrow \text{CBS}$ are accompanied by relatively small and steadily decreasing changes in the relative energies. Spectroscopic properties are sensitive to relative rather than absolute energies, so the latter are not reported in this and the following tables. Expansion of the Gaussian basis toward the CBS limit can either increase or decrease the relative energies at different parts of the PES. For example, at short symmetric distances (structures 2 and 4) basis set expansion results in smaller relative energies, while at extended symmetric configurations (structures 3 and 5) results in an increase in relative energies. It is important to observe that while basis set expansion almost always results in smooth changes, even the $6Z \rightarrow \text{CBS}$ correction can be as large as 43 cm^{-1} (structure 10).

The smooth behavior of the energies as n is systematically increased in the cc sets has been exploited by extrapo-

TABLE II. Convergence of valence-only relative energies as a function of basis set size for the ten reference structures given in Table I, presented relative to the nearly equilibrium structure 1. Energies are in wave numbers. The label+Q stands for the Davidson correction. See the text for the description of the 8×8 full-valence CAS reference space.

No.	cc-pVDZ					QZ	5Z	6Z	CBS	
	ICMRCI	ICMRCI+Q	MRCI	MR-AQCC	FCI				ICMRCI+Q	ICMRCI
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	2 058.9	2 065.5	2 067.5	2 071.5	2 060.8	1 691.9	1 664.8	1 660.7	1 657.0	1 631.3
3	18 106.2	18 066.4	18 063.4	18 038.4	18 102.8	19 037.3	19 125.3	19 136.2	19 151.8	19 304.3
4	34 314.2	34 338.7	34 342.3	34 357.2	34 324.8	31 966.4	31 817.6	31 786.5	31 755.1	31 668.8
5	31 141.2	31 082.6	31 084.0	31 047.9	31 143.5	32 668.6	32 782.6	32 806.4	32 833.0	33 055.9
6	12 370.8	12 380.6	12 378.2	12 383.6	12 368.0	10 864.1	10 840.9	10 821.7	10 795.9	10 833.8
7	28 996.6	28 958.2	28 984.7	28 963.2	28 972.6	28 103.6	28 085.0	28 077.4	28 069.9	28 115.6
8	26 829.6	26 826.1	26 815.0	26 811.5	26 819.5	24 637.3	24 636.1	24 621.3	24 599.1	24 715.0
9	18 297.2	18 277.6	18 277.4	18 265.2	18 294.3	18 193.2	18 218.4	18 223.9	18 231.0	18 309.7
10	34 892.9	34 845.3	34 858.1	34 830.1	34 910.7	37 080.2	37 176.4	37 209.7	37 252.7	37 393.8

lating the surface to the CBS, that is $n=\infty$, limit.^{39–43} The best three CASSCF energies were extrapolated using a three-parameter exponential form⁴³ as follows:

$$E_{\text{extr}}^{\text{CASSCF}} = \frac{E_{4Z}E_{6Z} - E_{5Z}^2}{E_{4Z} - 2E_{5Z} + E_{6Z}}, \quad (1)$$

while a simple two-parameter inverse cubic polynomial⁴² with the best two energies was used for the estimation of the CBS ICMRCI+ Q valence-only correlation energy,

$$E_{\text{extr}}^{\text{corr}} = \frac{5^3 E_{5Z} - 6^3 E_{6Z}}{5^3 - 6^3}. \quad (2)$$

The frozen-core ICMRCI+ Q model does not include the entire valence electron correlation energy. FCI calculations cannot presently be performed for water with basis sets considerably larger than about DZ (in the present case cc-pVDZ). Comparison of FCI and variants of ICMRCI and MRCI calculations at the cc-pVDZ level (Table II) show a comfortably small variation in the differences. It is notable that the closest agreement with FCI among the approximate treatments is exhibited by the uncorrected ICMRCI relative energies, where the differences barely exceed a few cm^{-1} even at about $35\,000\text{ cm}^{-1}$ above the PES minimum. Because the FCI–MRCI effect is small and probably cannot be modeled accurately at the DZ level (it would probably increase and change characteristics in most cases if larger basis sets were used for its evaluation), in the final calculations the ICMRCI+ Q energies have been utilized for extrapolation and estimating the valence-only CBS FCI limit.

B. Core correlation

Clearly,^{3,35,39} the largest error in the extrapolated CBS ICMRCI+ Q surface is due to electron correlation effects neglected by freezing the oxygen core orbital during the ICMRCI computations. Partridge and Schwenke (PS) computed a core correction surface³ for water at the not fully size-consistent ACPF (Ref. 18) level, which they denoted CV for core valence although in practice it allows for core-core correlation effects as well. They used a basis set derived from the cc-pVQZ basis set, augmented with tight and diffuse functions for both O and H, which they designated as CQZ. It is important to use a size-consistent method during determination of the core correction surface as it involves taking a difference of energies from eight- and ten-electron computations.

The core correlation corrections have been recomputed at the reference points of Table I using fully size-consistent single-reference coupled-cluster techniques^{25,44,45} and appropriate correlation-consistent Gaussian basis sets.⁴⁶ See Table III for the results. The final “best estimates” were obtained by an additivity assumption, i.e., by augmenting the CV6Z CCSD core corrections with CVQZ CCSDT–CCSD and CVTZ CCSDTQ–CCSDT corrections. The computationally most expensive part of the procedure is the determination of the all-electron CVTZ CCSDTQ energies.

It is noteworthy how sensitive the computed core corrections are both to increase in basis set size and electron correlation treatment. Clearly, the cc-pCVDZ basis is much too

small to predict reasonable core corrections. The CVQZ basis seems to be a good compromise in accuracy and cost. Nevertheless, extension of the basis from CV5Z to CV6Z still has a few cm^{-1} effect at the CCSD and CCSD(T) levels, though this should have rather small consequence on the variational computation of vibrational band origins (VBOs) and rotation term values. More noteworthy is the change when going from CCSDT to CCSDTQ. It seems that (a) higher-order correlation effects cannot be neglected during computation of core corrections; and (b) though the higher-order core corrections are small for most other (nonspectroscopic) applications, unfortunately, they increase with increase in the size of the basis. The data of Table III also suggest that PS’s CV surface reproduces the core correlation effects reliably. Therefore, the CV correction surface of Partridge and Schwenke³ was employed here and in our previous studies^{4,11} unchanged. Note that augmentation of the CBS ICMRCI+ Q PES with this core correction surface reduces the errors of the predicted VBOs by almost a factor of 3. It needs to be mentioned that while the valence-only energies were determined at the ten reference structures directly, the CV corrections as well as many of the other corrections presented in the next subsections were calculated on different grids; thus, their values at the reference structures could perhaps be spoiled slightly by the fitting procedure. Some of the reference geometries are also outside of the original range of the surfaces; therefore, the error introduced by the extrapolation can be significant. Finally, it is noted that error compensation resulting from the neglect of the FCI-ICMRCI+ Q valence only and the best estimate–CQZ ACPF core corrections does not seem to be prevalent.

C. Relativistic effects

The next most important correction to the electronic energies comes from the finite speed of light, not taken into account in nonrelativistic (valence-only or all-electron) treatments of the motions of the electrons. The inclusion of special relativity into electronic structure theory, which can formally be done using the Dirac Hamiltonian, gives rise to several effects.^{47–49} The dominant effect is a one-electron contribution arising directly and indirectly from the high velocity of the core electrons. We compute the resulting energy correction using first-order perturbation theory as a sum of the mass velocity and Darwin terms.⁴⁷ The relevant data are given in Table IV.

The one-electron mass-velocity and Darwin (MVD1) correction surface usually gives the majority of the relativistic energy correction for closed-shell molecules comprised of light elements. In this study the MVD1 surface derived previously¹⁹ was extended to slightly higher energies, by calculating extra 63 points in addition to the original grid of 325 points. The extra points, similarly to the original ones, were calculated at the cc-pVQZ CCSD(T) level of theory. Comparisons with full Dirac Hamiltonian calculations of Quiney *et al.*,⁵⁰ who used small basis sets and less accurate wave functions, showed differences in the magnitude of this correction but excellent agreement in its variation with geometry, which is the key property for spectroscopy. The usually

TABLE III. Core corrections to the valence-only BO energy, relative to a nearly equilibrium structure (1 of Table I), computed at different levels of coupled cluster theory.

No.	CQZ		CVDZ			CVTZ			CVQZ			CV5Z			CV6Z			Best estim. ^b	
	ACPF ^a	CCSD	CCSD(T)	CCSDT	CCSDTQ	CCSD	CCSD(T)	CCSDT	CCSDTQ	CCSD	CCSD(T)	CCSDT	CCSD	CCSD(T)	CCSDT	CCSD	CCSD(T)		CCSDT
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	-46.9	-27.6	-26.5	-26.4	-26.4	-40.2	-37.0	-36.5	-36.4	-46.7	-43.2	-42.7	-48.3	-44.7	-49.1	-49.1	-45.4	-44.7	-44.7
3	147.9	80.7	70.6	70.2	69.7	141.2	117.8	114.0	112.8	158.9	133.5	129.2	163.9	137.8	166.3	166.3	140.0	134.5	134.5
4	-212.2	-118.8	-115.6	-115.5	-115.3	-181.0	-171.3	-169.8	-169.4	-207.8	-196.9	-195.3	-216.5	-205.2	-220.0	-220.0	-208.6	-206.5	-206.5
5	185.9	101.3	81.7	80.8	80.0	194.8	152.3	144.5	142.5	214.7	169.0	160.2	221.2	174.6	224.3	224.3	177.2	166.4	166.4
6	-84.9	-18.2	-18.0	-17.9	-18.0	-75.5	-74.2	-72.8	-73.5	-81.9	-80.9	-79.0	-83.0	-82.2	-83.8	-83.8	-83.0	-81.8	-81.8
7	35.4	15.5	15.5	15.6	15.5	29.5	28.1	28.7	28.3	31.7	30.3	31.0	31.6	30.4	31.8	31.8	30.6	30.9	30.9
8	-18.4	14.9	12.3	12.4	12.0	-18.9	-24.4	-22.8	...	-17.0	-23.8	-21.3	-14.8	-22.4	-14.2	-20.3	-20.3
9	36.2	20.6	14.2	14.0	13.7	44.2	31.0	28.9	...	45.9	32.5	30.1	47.8	33.4	48.4	48.4	...	30.8	30.8
10	89.3	94.5	48.0	48.8	47.5	185.0	100.2	82.1	...	199.1	111.5	88.3	203.2	115.7	205.3	205.3	...	91.1	91.1

^aData of this column are taken from Ref. 3. The basis set CQZ is derived from the cc-pVQZ set with extra diffuse and tight functions (Ref. 3).

^bDetermined using additivity assumptions. For structures 1–7, the best estimates are determined as CV6Z CCSD(T)+(CVQZ CCSD(T)+CCSDT)–CCSD(T)–CCSDT. For structures 8–10, the best estimates are determined as CV5Z CCSD(T)+(CVQZ CCSD(T)+CCSDT)–CCSD(T)–CCSDT.

TABLE IV. Relativistic energy corrections to the all-electron BO energy, relative to a nearly equilibrium structure (1 of Table I). See text for details of the computations.

No.	MVD1	D2	Breit	QED	Total
1	0.00	0.00	0.00	0.00	0.00
2	-0.44	-0.56	5.70	-0.27	4.43
3	-29.44	0.39	-15.67	1.86	-42.86
4	-29.74	-3.94	28.40	-0.39	-5.67
5	-49.74	-3.14	-18.88	2.95	-68.81
6	53.77	2.67	2.50	-2.64	56.30
7	-37.76	-2.11	1.62	1.55	-36.71
8	53.24	4.11	-5.73	-2.37	49.24
9	-19.64	-0.39	-3.33	0.83	-22.52
10	-46.12	-1.09	-12.35	-10.53	-70.08

rather small, two-electron contribution to the Darwin term (D2),⁴⁹ was also included in the relativistic corrections.²⁰

The Coulomb interaction, due to its instantaneous character, is not consistent with special relativity and needs to be supplemented by the Breit interaction.⁴⁸ Since the D2 and Breit correction surfaces were used without modification, no further discussion is given here. It is only mentioned that the surfaces were obtained using a grid and energy range considerably more limited than those employed for V_{CBS} .

The lowest-order quantum electrodynamic effect, the one-electron Lamb shift, was modeled using the prescription of Pyykkö *et al.*²⁴ We know of no case where the use of QED has had any impact on molecular physics. However, our calculations are of such accuracy that incorporating this effect leads to a clear, systematic improvement in the predictions of rovibrational transitions. Since this correction surface²⁴ was used without modification, no further discussion of it is given here. It is only mentioned that the surface was obtained using a limited grid and energy range and a simple polynomial fit, making the resulting correction surface inappropriate at high-energy regions of the global PES of water. Consequently, it is not surprising that the QED correction for reference point 10 appears to be much too large (Table IV).

D. Beyond the BO separation of electronic and nuclear motions

Thus far the treatment has remained within the framework of the Born-Oppenheimer (BO) approximation. Corrections to the BO approximation can be obtained by means of a second-order contact transformation method pioneered by Bunker and Moss.⁵¹ This introduces two terms: (a) the simple first-order DBOC, which allows for the action of the nuclear motion kinetic energy operator on the ground-state electronic wave functions and gives rise to a mass-dependent correction to the PES; and (b) the considerably more difficult second-order (so-called nonadiabatic) correction, which introduces coupling between electronic states and primarily results in corrections to the kinetic energy operator to be employed in the nuclear motion calculations.

During this work mass-dependent DBOC surfaces, computed previously⁵² using MRCI wave functions and the cc-pVTZ basis set, were utilized for the major isotopologues of water considered (see Table V for these PES corrections for

TABLE V. Diagonal Born-Oppenheimer corrections (DBOCs) for four isotopologues of water, relative to a nearly equilibrium structure (1 of Table I), obtained at the cc-pVTZ MRCI (MRCI, Ref. 52) and frozen-core aug-cc-pVTZ CISD (CISD, this work) levels.

No.	H ₂ ¹⁶ O		H ₂ ¹⁷ O		H ₂ ¹⁸ O		D ₂ ¹⁶ O	
	MRCI	CISD	MRCI	CISD	MRCI	CISD	MRCI	CISD
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	2.7	3.0	2.7	3.0	2.7	3.0	1.2	1.6
3	-0.5	-4.4	-0.6	-4.5	-0.7	-4.5	0.8	-1.8
4	17.1	17.6	16.9	17.6	16.7	17.5	10.4	9.4
5	4.6	-3.3	4.5	-3.4	4.3	-3.4	3.6	-1.0
6	-14.1	-14.1	-14.1	-14.1	-14.1	-14.1	-6.9	-7.0
7	18.5	19.3	18.4	19.2	18.3	19.1	10.5	10.5
8	-1.6	-6.9	-1.7	-7.0	-1.8	-7.1	0.3	-2.8
9	5.8	2.7	5.7	2.7	5.7	2.6	3.3	1.6
10	28.3	9.7	28.2	9.6	28.1	9.5	15.5	5.5

four symmetric isotopologues of water). The values for the different nuclear masses used in this work are 15.990 526, 16.994 743, 17.994 771, 1.007 276, and 2.013 553 u for ¹⁶O, ¹⁷O, ¹⁸O, H, and D, respectively. The DBOC surfaces change considerably for the different isotopologues, the corrections for D₂O being significantly smaller than for the H-containing isotopologues. The differences of the corrections among the isotopologues are reproduced reasonably well but not excellently at the frozen-core aug-cc-pVTZ CISD level, where CISD stands for a CI treatment with all single and double excitations.

DBOCs for H₂¹⁶O computed at different levels of electronic structure theory are presented in Table VI. It is clear that relatively small basis sets, even the aug-cc-pVDZ set, seem to be sufficient to compute reliable DBOC surfaces. This slight basis set dependence of the DBOCs at a given level is possibly due to the fact that the DBOC is an expectation value, through the basis functions, of a one-body operator, and such expectation values usually converge quickly. On the other hand, inclusion of electron correlation seems to be important for the proper description of the DBOC effects over the PES of water. Most importantly, while DBOCs computed at the Hartree-Fock level are seemingly correct along the bending motion, they give even qualitatively wrong be-

havior when the molecule is stretched. This is not surprising and was pointed out before by Schwenke.⁵² Results from the small number of test calculations presented in Table V confirm the accuracy of the DBOC surfaces computed by Schwenke⁵² and utilized in this study without change.

Two methods of including nonadiabatic corrections to the vibrational motion were explored in Ref. 4. The method of Schwenke⁵³ involving explicit coupling of the ground electronic state to electronically excited states was compared to a much simpler, two-term adjustment of the vibrational kinetic energy operator using parameters taken from Schwenke's study.¹⁰ The results of the two methods agree to better than 0.1 cm⁻¹. These treatments are only valid for energies up to 10 000 cm⁻¹ and their effect is small, see Ref. 4. Vibrational nonadiabatic effects have therefore not been included in our final calculations. Rotational nonadiabatic corrections are, however, non-negligible for high values of the rotational quantum number, *J*. Again the full⁵³ and the reduced¹⁰ method of including this correction gave very similar results;⁴ the latter is used for the present calculations.

III. FITTING THE SURFACES

To use the *ab initio* data points computed over a grid most efficiently in nuclear motion calculations we need to fit

TABLE VI. Diagonal Born-Oppenheimer correction (DBOCs) computed at different levels of theory for H₂¹⁶O relative to a nearly equilibrium structure (1 of Table I). The basis sets indicated are *anZ*=aug-cc-p*nZ* (*n*=D, T, and Q).

No.	cc-pVTZ	aDZ			aTZ		aQZ
	ICMRCI ^a	HF	CISD	CISDT	HF	CISD	HF
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	2.7	2.9	2.9	2.9	2.9	3.0	2.9
3	-0.5	-6.7	-4.8	-3.6	-5.7	-4.4	-5.9
4	17.1	15.9	16.5	16.2	16.8	17.6	16.5
5	4.6	-6.9	-3.4	-1.1	-5.7	-3.3	-5.8
6	-14.1	-14.2	-13.9	-14.0	-14.5	-14.1	-14.6
7	18.5	21.6	18.3	17.9	22.1	19.3	22.1
8	-1.6	-9.6	-5.8	...	-10.0	-6.9	-10.1
9	5.8	0.2	2.4	...	1.0	2.7	0.8
10	28.3	0.9	11.2	...	1.6	9.7	1.5

^aData of this column from Ref. 52.

them to analytical surfaces. In the present study these surfaces are implemented as FORTRAN codes and their final form is given in the Supplementary Material. Fitting the surfaces involves several delicate choices if the high quality of the underlying *ab initio* calculations is not to be lost.

The adiabatic CVRQD PES for even isotopologues of water can be expressed as a sum of seven surfaces,

$$V = V_{\text{CBS}} + V_{\text{CV}} + V_{\text{MVD1}} + V_{\text{D2}} + V_{\text{Breit}} + V_{\text{QED}} + V_{\text{DBOC}}, \quad (3)$$

where V_{CBS} represents the extrapolated valence-only CBS energies (Sec. II A), V_{CV} represents the core-core and core-valence interactions (Sec. II B), V_{MVD1} contains the first-order electronic relativistic corrections (Sec. II C), V_{D2} and V_{Breit} are second-order relativistic corrections (Sec. II C), V_{QED} accounts for the lowest-order quantum electrodynamic effect (the one-electron Lamb shift, Sec. II D), and finally, V_{DBOC} is the Born-Oppenheimer diagonal correction (Sec. II E), making the resulting surfaces mass and therefore isotopologue dependent. All the different data points had the same weight in the final fitting procedure.

A. Correction surfaces

As discussed in Sec. II, some of the correction surfaces have already been published in detail, so they need not be discussed again: V_{CV} is taken from Ref. 3, V_{D2} and V_{Breit} from Ref. 20, and V_{QED} from Ref. 24. The other correction surfaces have been fitted to the respective data points using standard least-squares techniques together with polynomial expansions about an assumed equilibrium structure which in bond length-bond angle coordinates is represented by (r_e, r_e, θ_e) .

The fits of the CVRQD PESs are based on the use of symmetry coordinates

$$s_1 = (r_1 + r_2)/2 - r_e \quad (4)$$

and

$$s_2 = (r_1 - r_2)/2. \quad (5)$$

For V_{CBS} and V_{MVD1} the angular displacements are represented using the so-called Jensen coordinate,

$$s_3 = \cos \theta - \cos \theta_e, \quad (6)$$

which ensures the correct saddle point behavior of these surfaces at linear geometries. (Note that due to the particular smoothness of the V_{Breit} and V_{Darwin} surfaces, their fits used the simpler angular coordinate $s_3 = \theta - \theta_e$). The generic surface V_X can thus be written as

$$V_X = \sum_{ijk}^N c_{ijk} s_1^i s_2^j s_3^k, \quad (7)$$

where i , j , and k assume non-negative values.

The correction surfaces V_{MVD1} , V_{D2} , and V_{DBOC} are smooth functions of the internal coordinates, meaning that their fitting does not display significant difficulties.

The data set used to determine V_{MVD1} comprises 388 points. The surface was fitted using 55 terms, the standard deviation for the fit being 0.13 cm^{-1} . (Note that the surfaces

V_{Breit} and V_{D2} were fitted to a smaller set of 325 points using 55 terms, and a standard deviation smaller than 0.04 cm^{-1} .)

The Born-Oppenheimer diagonal correction V_{DBOC} is the only term in Eq. (3) dependent on the nuclear masses. Thus different surfaces were produced for different water isotopologues. For the main water isotopologue (H_2^{16}O), 336 data points were fitted with 118 parameters, resulting in a standard deviation of 0.031 cm^{-1} ; for H_2^{18}O , 338 data points were fitted using 86 parameters giving a standard deviation of 0.084 cm^{-1} .

B. Valence-only surface

Fitting the V_{CBS} surface is particularly difficult due to the complexity of this surface, and thus has to be done with particular care. The surface must reproduce the strong repulsion at short internuclear distances, the attractive part near the equilibrium geometry, the barrier to linearity, and the first dissociative channel, while special attention is required for linear geometries, where the surface has a saddle point. The largest residues in the fits arise from points in the nearly linear region.

Our choice of functional form for V_{CBS} followed the work of PS,³ to which we refer for precise definitions,

$$V_{\text{CBS}}(r_1, r_2, \theta) = V^a(r_1) + V^a(r_2) + V^b(r_{\text{HH}}) + V^c(r_1, r_2, \theta), \quad (8)$$

where r_{HH} is the HH distance. The two-body potentials in Eq. (8) are defined as

$$V^b(r) = A \exp(-br), \quad (9)$$

and

$$V^a(r) = DW(r)(1 - \mathcal{Y}(r)) + D_e W(r)\mathcal{Y}(r), \quad (10)$$

where

$$W(r) = \exp[-2a(r - r_0)] - 2 \exp[-a(r - r_0)] \quad (11)$$

and \mathcal{Y} is a switching function

$$\mathcal{Y}(r) = \{1 + \exp[d(x_0 - r)]\}^{-1}. \quad (12)$$

The complicated form for V^a was found to be effective for the fitting procedure; it relaxes the constraint on the dissociation limit for our surface, which is manipulated through the parameter D .

The three-body part of the surface is given by V^c ,

$$V^c(r_1, r_2, \theta) = c_{000} + \left(\sum_{ijk}^{N_p} c_{ijk} s_1^i s_2^j s_3^k \right) \times \exp\{-\beta[(r_1 - r_e)^2 + (r_2 - r_e)^2]\}, \quad (13)$$

where s_1 , s_2 , and s_3 are given by Eqs. (4)–(6).

The number of linear parameters to optimize in V_{CBS} is $N_p + 3$, where N_p is the number of polynomials introduced in the expansion of Eq. (13), and the three other linear parameters are A in Eq. (9), D in Eq. (10), and c_{000} in Eq. (13). For the nonlinear parameters we use the same values as in PS, with the exception of b in Eq. (9). For symmetry reasons, only even values for j are allowed in Eq. (13). The optimum values of the fitted coefficients are not given explicitly; they

TABLE VII. History of *ab initio* computed and empirical barriers to linearity for water (H_2^{16}O).

Reference	Method	Year	Barrier
59	Spectroscopic empirical	1987	11 493
60	Spectroscopic empirical	1989	11 246
61	Spectroscopic empirical	1996	10 966
62	Effective Hamiltonian	1996	11 154
3	<i>Ab initio</i>	1997	11 155
3 +adiabatic+relativistic corr. (Ref. 39)	<i>Ab initio</i>	1997	11 192
3	Semitheoretical	1997	11 128
39	Focal-point approach (Ref. 39)	1998	11 046±70
64	Focal-point approach (Ref. 39)	1999	11 127±35
63	Semitheoretical	2000	11 105±5
40	Focal-point approach (Ref. 39)	2001	11 119±12
4	Focal-point approach (Ref. 39)	2003	11 123±5
65	Fit to emission spectra	2005	11 114±5
66	Semitheoretical	2006	11 129.2
This work	<i>Ab initio</i>	2006	11 123.3

can be retrieved from the FORTRAN codes representing the four PESs given in the electronic archive.¹²

IV. NUCLEAR MOTION COMPUTATIONS

To make direct comparisons with experiment a series of variational rotation-vibration calculations was performed using the CVRQD PESs. These computations utilized the DVR3D program suite⁵⁴ and previously tested basis sets.⁵⁵ DVR3D was adapted to allow for the effects of rotational nonadiabatic effects. All nuclear motion calculations used nuclear masses, the preferred choice when mass-dependent adiabatic surfaces are available. The variational method employed, without the nonadiabatic corrections, has previously been shown⁴ to give energies which agree within 0.01 cm^{-1} with other procedures for treating the nuclear motion problem.⁵⁶ Furthermore, the nuclear motion calculations, again without the nonadiabatic corrections, with the PESs of this study have been checked against computations with the DOPI3R code,^{9,57} employing substantially different algorithm and basis sets. The two sets of results were found to be identical to better than 0.01 cm^{-1} . In contrast to the electronic structure calculations, all nuclear motion calculations presented here were performed on desktop computers.

V. SELECTED CHARACTERISTICS OF THE CVRQD SURFACES

A. Equilibrium and effective structures

Equilibrium structures are fundamental entities yet they are usually inferred from experimental data by complicated procedures which often rely on several assumptions, including the Born-Oppenheimer approximation. Theory provides a direct albeit still cumbersome route to equilibrium structures if all relevant effects, perhaps through approximate corrections, are taken into account.¹¹

The compound surface CVRQD gives the adiabatic equilibrium structure of H_2^{16}O as an OH bond length of 0.95785 \AA and a bond angle of 104.50° .¹¹ The corresponding mass-independent (BO) equilibrium bond length and bond angle are $r_e^{\text{BO}}=0.95782 \text{ \AA}$ and $\theta_e^{\text{BO}}=104.483^\circ$. Clearly,

the differences are very small, though meaningful at the level of accuracy of the computations of this study. The concept of mass-independent equilibrium structures seems to be valid to about $3 \times 10^{-5} \text{ \AA}$ and 0.02° for water. It is believed that the equilibrium structural parameters should be nearly exact both in the Born-Oppenheimer and adiabatic limits; conservative error limits are 0.00010 \AA and 0.010° .

The variational nuclear motion calculations of this study also allowed for obtaining accurate temperature-dependent effective structures.⁵⁸ At 0 K the vibrationally averaged r_g bond lengths of H_2^{16}O and D_2^{16}O are 0.97565 and 0.97077 \AA , respectively. The minuscule difference in the equilibrium OH and OD bond lengths thus becomes, due to vibrational averaging, almost 0.005 \AA .

B. Barrier to linearity

An interesting quantity characterizing the ground-state PES for water is its barrier to linearity. There have been a variety of attempts^{3,4,39,40,59-66} to determine this quantity; they are summarized in Table VII. Due partly to efforts of the authors of this paper, during the last few years a consensus has emerged between computed and empirical values. The optimum OH bond length at the linear structure is 0.93323 \AA , showing a substantial contraction compared to the bent equilibrium value due to rehybridization at the O center.

The barrier to linearity is not directly accessible to spectroscopy; however, a very recent study⁶⁵ based on water emission lines recorded in an oxyacetylene spectrum⁶⁷ has, for the first time, identified transitions associated with highly bending states which sample this barrier. Fits to this spectrum give a barrier height of $11114 \pm 5 \text{ cm}^{-1}$ for H_2^{16}O , which is marginally consistent with the value given by the CVRQD surface, 11123.3 cm^{-1} .

At this point it is of interest to point out a particular problem with the *ab initio* PES due to Partridge and Schwenke.³ In order to make their computations feasible on computers available to them a decade ago, PS deleted certain functions from the correlation-consistent basis set with $n=5$. This resulted in problems reflected in their barrier height

reported in Table VII and also in their bending correction curve. The empirical corrections determined by Kain *et al.*⁶³ to the PS bending curve are almost the same as the correction obtained after reintroducing the missing Gaussian basis functions into the electronic structure calculations. This effect can be understood by noting that the linear structure has inversion symmetry, hence basis functions with odd and even l will contribute and mix differently than at the nonlinear equilibrium structure.

C. Anharmonic force fields

The simplest way to avoid the difficulties arising from the exceedingly large number of grid points needed to be computed for four-atomic and larger systems to represent their PESs is the expansion of the potential in a Taylor series about a reference, usually the equilibrium, structure. While three-atomic molecules do not present an overwhelming problem in this respect, it is still interesting to obtain force field representations for the different isotopologues of water at the very high accuracy represented by the CVRQD PESs. The force field expansions up to sixth order are presented in Table VIII for the usual four isotopologues treated in this study, H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, and D₂¹⁶O.

Since the CVRQD PESs are composed of several parts of complicated numerical form, we have used a Lagrange interpolation technique⁶⁸ to obtain the required derivatives. A grid of 21 points was employed in each dimension; the step sizes were 0.01 Å in r_1 and r_2 and 0.01 rad in θ .

The force fields should be considered very accurate at least up to fourth order. This can also be judged from their comparison with the best previous anharmonic force fields.^{2,8,39} Due to numerical problems some of the higher-order off-diagonal force constants may be inaccurate but this should not strongly affect results from variational rovibrational calculations employing them.

D. Harmonic frequencies, vibrational fundamentals, and zero-point energy

The harmonic vibrational frequencies that can be obtained from the adiabatic quadratic force fields presented in Table VIII are as follows: for H₂¹⁶O $\omega_1=3833.0$, $\omega_2=1648.8$, and $\omega_3=3944.1$; for H₂¹⁷O $\omega_1=3828.7$, $\omega_2=1645.2$, and $\omega_3=3935.5$; for H₂¹⁸O $\omega_1=3824.9$, $\omega_2=1641.9$, and $\omega_3=3928.0$; and for D₂¹⁶O $\omega_1=2763.0$, $\omega_2=1207.3$, and $\omega_3=2889.9$. These harmonic frequencies can be considered as the best *ab initio* estimates of these quantities up to date.

Table IX summarizes how *ab initio* predictions¹⁻⁸ of the fundamental vibrational frequencies of water have changed with time. It is noteworthy that at a particular reference structure and particular level of theory force field expansions⁶⁹ can be highly accurate (see, e.g., the results of Martin *et al.*⁸ and Császár and Mills²). This accuracy, however, will quickly be lost at even slightly higher regions of the spectrum.

The zero-point energies (ZPEs) of the water isotopologues play an important role in many areas of physical chemistry, including thermochemistry. The highly accurate

variational nuclear motion calculations performed as part of this study with the CVRQD PESs yield excellent estimates for ZPEs; they are 4638.31, 4630.37, 4623.32, and 3389.96 cm⁻¹ for H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, and D₂¹⁶O, respectively.

E. Vibrational band origins (VBOs)

The accuracy with which the observed VBOs of H₂¹⁶O are reproduced by the CVRQD PES can be deduced from the data given in Table X. It is clear from the table that the lower levels are reproduced more accurately and that the fully symmetric computed VBOs have a slightly higher accuracy. It must also be noted that the use of the valence-only aug-cc-pV6Z ICMRCI+ Q surface plus corrections given above still give residual errors of up to 7 cm⁻¹ in the VBOs and a standard deviation for all VBOs, σ , of 1.85 cm⁻¹.

As shown in Table I of Ref. 4 and can be deduced from the tables presented here, to achieve sub-wave-number accuracy in the prediction of VBOs it is (a) necessary not only to use large basis sets in the electronic structure computations but also to extrapolate to the CBS limit; (b) necessary to augment the valence-only CBS MRCI PES with the CV correction surface, since this reduces the errors of the predicted VBOs by almost a factor of 3; and (c) important to include also a number of terms normally neglected in standard electronic structure calculations. As it can be deduced from the last row of Table X, each of the correction terms has a significant effect on improving the correspondence between observed and calculated levels. For example, the QED term has a total effect of 0.4 cm⁻¹ on the standard deviation for the VBOs.

F. Rotational term values

As detailed in Table III of Ref. 11, the CVRQD adiabatic PESs excellently reproduce the lowest rotational levels ($J=1$ and 2) for the isotopologues of water considered, H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, and D₂¹⁶O. The $J=1$ term values deviate from the experimentally determined ones⁷⁰⁻⁷³ by less than 0.001 cm⁻¹. The maximum deviation for the $J=2$ CVRQD term values is 0.003 cm⁻¹. The related mean and maximum deviations for the fitted potential of Ref. 66, obtained through elaborate adjustment of the CVRQD PESs to all observed rovibrational levels of several isotopologues of water to better than 0.05 cm⁻¹, are very similar. Many of the $J=2$ CVRQD and fitted variational results bracket the experimental term values.

Precision of the *ab initio* prediction of higher J transitions by the CVRQD PESs is exceptionally good, as well. Results for the $J=20$ rotational levels are presented in Table XI for the first four VBOs of H₂¹⁶O. The computed results are accurate and, as expected in the case of an *ab initio* PES, the differences are systematic to a high degree allowing the use of the computed information in assignment of yet unknown term values. Inclusion of rotational nonadiabaticity seems to worsen the agreement between theory and experiment, as it can be seen from the last column of Table XI.

TABLE VIII. Force constants (FCs) $\partial^{(n_1+n_2+n_\theta)}V(r_1, r_2, \theta) / \partial r_1^{n_1} \partial r_2^{n_2} \partial \theta^{n_\theta}$ of the potential energy surfaces CVRQD of four major isotopologues of water, H_2^{16}O , H_2^{17}O , H_2^{18}O , and D_2^{16}O , calculated at their respective minima, up to sixth order. Units are $\text{aJ } \text{\AA}^{-(n_1+n_2)} \text{rad}^{-n_\theta}$.

n_1	n_2	n_θ	FC ^a	n_1	n_2	n_θ	FC ^a	n_1	n_2	n_θ	FC ^a
H_2^{16}O											
0	0	1	0.0000	1	0	0	0.0000	0	0	2	0.7025
1	0	1	0.2580	1	1	0	-0.1025	2	0	0	8.4597
0	0	3	-0.7114	1	0	2	-0.3174	1	1	1	-0.5101
2	0	1	-0.1167	2	1	0	-0.0517	3	0	0	-58.6838
0	0	4	-0.6877	1	0	3	0.7287	1	1	2	0.6089
2	0	2	-0.2101	2	1	1	0.3560	2	2	0	0.6387
3	0	1	-1.4332	3	1	0	-0.7677	4	0	0	362.572
0	0	5	-1.4257	1	0	4	0.2206	1	1	3	0.0586
2	0	3	2.0571	2	1	2	-0.8018	2	2	1	-0.8777
3	0	2	0.9128	3	1	1	2.0248	3	2	0	2.5443
4	0	1	2.9871	4	1	0	3.0719	5	0	0	-2398.04
0	0	6	5.0060	1	0	5	1.1656	1	1	4	-1.4305
2	0	4	6.6162	2	1	3	-1.7836	2	2	2	-5.5976
3	0	3	3.6675	3	1	2	3.1141	3	2	1	2.6569
3	3	0	68.4877	4	0	2	-1.7944	4	1	1	-9.6200
4	2	0	-91.9667	5	0	1	1.5432	5	1	0	70.8015
6	0	0	18 157.04								
H_2^{17}O											
0	0	1	0.0000	1	0	0	0.0000	0	0	2	0.7024
1	0	1	0.2580	1	1	0	-0.1025	2	0	0	8.4597
0	0	3	-0.7111	1	0	2	-0.3173	1	1	1	-0.5100
2	0	1	-0.1166	2	1	0	-0.0520	3	0	0	-58.6838
0	0	4	-0.6855	1	0	3	0.7299	1	1	2	0.6088
2	0	2	-0.2098	2	1	1	0.3556	2	2	0	0.6383
3	0	1	-1.4336	3	1	0	-0.7682	4	0	0	362.570
0	0	5	-1.4509	1	0	4	0.2123	1	1	3	0.0547
2	0	3	2.0509	2	1	2	-0.8004	2	2	1	-0.8692
3	0	2	0.9088	3	1	1	2.0272	3	2	0	2.5706
4	0	1	2.9958	4	1	0	3.1212	5	0	0	-2398.05
0	0	6	4.8750	1	0	5	1.1065	1	1	4	-1.4331
2	0	4	6.5895	2	1	3	-1.7811	2	2	2	-5.5787
3	0	3	3.6674	3	1	2	3.1232	3	2	1	2.6776
3	3	0	68.2158	4	0	2	-1.7739	4	1	1	-9.6147
4	2	0	-92.3466	5	0	1	1.5385	5	1	0	70.3124
6	0	0	18 157.56								
H_2^{18}O											
0	0	1	0.0000	1	0	0	0.0000	0	0	2	0.7024
1	0	1	0.2579	1	1	0	-0.1025	2	0	0	8.4596
0	0	3	-0.7108	1	0	2	-0.3172	1	1	1	-0.5099
2	0	1	-0.1166	2	1	0	-0.0523	3	0	0	-58.6832
0	0	4	-0.6836	1	0	3	0.7309	1	1	2	0.6087
2	0	2	-0.2095	2	1	1	0.3551	2	2	0	0.6380
3	0	1	-1.4341	3	1	0	-0.7687	4	0	0	362.569
0	0	5	-1.4733	1	0	4	0.2049	1	1	3	0.0512
2	0	3	2.0454	2	1	2	-0.7991	2	2	1	-0.8616
3	0	2	0.9053	3	1	1	2.0293	3	2	0	2.5938
4	0	1	3.0034	4	1	0	3.1649	5	0	0	-2398.06
0	0	6	4.7593	1	0	5	1.0547	1	1	4	-1.4315
2	0	4	6.5664	2	1	3	-1.7783	2	2	2	-5.5532
3	0	3	3.6646	3	1	2	3.1392	3	2	1	2.6885
3	3	0	68.0350	4	0	2	-1.7478	4	1	1	-9.6102
4	2	0	-92.5138	5	0	1	1.5141	5	1	0	69.9389
6	0	0	18 157.11								

TABLE VIII. (Continued.)

n_1	n_2	n_θ	FC ^a	n_1	n_2	n_θ	FC ^a	n_1	n_2	n_θ	FC ^a
D ₂ ¹⁶ O											
0	0	1	0.0000	1	0	0	0.0000	0	0	2	0.7029
1	0	1	0.2581	1	1	0	-0.1025	2	0	0	8.4594
0	0	3	-0.7139	1	0	2	-0.3189	1	1	1	-0.5112
2	0	1	-0.1173	2	1	0	-0.0497	3	0	0	-58.6882
0	0	4	-0.7052	1	0	3	0.7205	1	1	2	0.6106
2	0	2	-0.2132	2	1	1	0.3610	2	2	0	0.6444
3	0	1	-1.4293	3	1	0	-0.7584	4	0	0	362.598
0	0	5	-1.2092	1	0	4	0.2937	1	1	3	0.0910
2	0	3	2.1080	2	1	2	-0.8159	2	2	1	-0.9537
3	0	2	0.9383	3	1	1	1.9997	3	2	0	2.3547
4	0	1	2.8988	4	1	0	2.6819	5	0	0	-2398.16
0	0	6	6.0033	1	0	5	1.6098	1	1	4	-1.4283
2	0	4	6.8096	2	1	3	-1.8456	2	2	2	-5.8559
3	0	3	3.6002	3	1	2	2.9965	3	2	1	2.4933
3	3	0	69.9637	4	0	2	-2.0402	4	1	1	-9.6964
4	2	0	-90.8088	5	0	1	1.6788	5	1	0	74.0286
6	0	0	18 158.67								

^aThe equilibrium structures at which the FCs have been evaluated are $r_1=r_2=0.957\ 854\ \text{\AA}$ and $\theta=104.5000\ \text{deg}$ for H₂¹⁶O, $r_1=r_2=0.957\ 854\ \text{\AA}$ and $\theta=104.5002\ \text{deg}$ for H₂¹⁷O, $r_1=r_2=0.957\ 854\ \text{\AA}$ and $\theta=104.5004\ \text{deg}$ for H₂¹⁸O, and $r_1=r_2=0.957\ 834\ \text{\AA}$ and $\theta=104.4903\ \text{deg}$ for D₂¹⁶O.

G. Limitations of the CVQRD surfaces

The importance of all different contributions needed to achieve the excellent predictions for the VBOs and the rotational term values presented in the previous subsections can be best summarized by looking at the standard deviations between observed and calculated values. If one considers only the valence PES, the standard deviation for all VBOs reported in Table X is $16.41\ \text{cm}^{-1}$, which drops substantially to $7.96\ \text{cm}^{-1}$ when the core corrections are added, and further reduces to 4.23, 3.83, and 1.90 when the relativistic correction, QED correction, and DBOC are included, in order.

Despite all of our efforts, there is still a discrepancy of almost $2\ \text{cm}^{-1}$ between observed and calculated VBOs on average for H₂¹⁶O, and for several VBOs the discrepancy of the *ab initio* predictions can be as high as $6\ \text{cm}^{-1}$. We are thus interested in examining in detail the differences between observed and calculated VBOs in order to understand the

limitations of the CVQRD surfaces, and to have a qualitative idea which part of the complex *ab initio* procedure needs to be revised and improved.

A useful tool available for our analysis is given by the spectroscopically determined FIS3 water surface of Ref. 66 which reproduces thousands of experimental levels for water over a wide energy range with an accuracy better than $0.1\ \text{cm}^{-1}$. This surface, whose construction was based on the CVQRD PESs, also allows for very high J rotational terms (up to $J=40$) to be predicted with excellent agreement with the available experimental values.⁶⁷ It is obvious that a semi-empirical surface is biased because it tries to mimic nonadiabatic BO effects, which cannot be described in terms of a single PES, within the PES itself. Nevertheless, neglecting nonadiabatic BO corrections is expected to introduce a much smaller error than the discrepancy between the observed and calculated values in Table X.

An analysis of Table X shows that the lower-energy

TABLE IX. Summary of *ab initio* computed fundamental frequencies for water (H₂¹⁶O). For a description of each method see the cited references. Type=type of PES, HFF=harmonic force field, and QFF=quartic force field in internal coordinates.

Reference	Method	Year	Type	ν_1	ν_2	ν_3
5	SCF	1974	HFF	4045	1728	4139
6	MBPT	1979		3702	1610	3789
7	CASSCF	1982		3691	1645	3794
8	QCISD(T)	1992	QFF	3657	1595	3756
2	CCSD(T)	1997	QFF	3657.7	1595.9	3754.6
1	MR-CISD	1997		3650.5	1604.6	3746.9
3	MRCI	1997	PES	3660.5	1597.4	3758.2
This work	CBS+CV	2006	PES	3660.10	1594.27	3758.76
This work	CVRQD	2006	PES	3656.33	1595.02	3754.98
Obs. 70				3657.05	1594.75	3755.93

TABLE X. Accuracy to which the observed vibrational band origins (VBOs) for H₂¹⁶O are reproduced by the CVRQD PES. The differences, in cm⁻¹, are given as observed–calculated. Note that the energy levels are given relative to the ZPE of H₂¹⁶O. See Sec. II for the description of the V=valence only, CV=all electron, CVR=CV+relativistic, CVRQ=CVR+QED, and the full CVRQD PESs.

(n_1, n_2, n_3)	Obs. ^a	V	CV	CVR	CVRQ	CVRQD
(010)	1 594.746	-0.325	0.481	-0.813	-0.754	-0.329
(020)	3 151.630	-0.791	1.160	-1.577	-1.451	-0.566
(100)	3 657.053	4.199	-3.051	0.414	0.279	0.004
(030)	4 666.791	-1.527	2.056	-2.373	-2.167	-0.783
(110)	5 234.975	3.796	-2.772	-0.537	-0.615	-0.519
(040)	6 134.015	-2.744	3.204	-3.312	-3.010	-1.066
(120)	6 775.093	3.320	-2.239	-1.354	-1.368	-0.872
(200)	7 201.540	8.715	-5.649	1.282	1.014	0.347
(002)	7 445.045	9.307	-5.906	1.324	1.042	0.161
(050)	7 542.437	-4.721	4.826	-4.461	-4.032	-1.420
(130)	8 273.977	2.674	-1.378	-2.100	-2.038	-1.105
(210)	8 761.579	8.280	-5.534	0.239	0.024	-0.341
(060)	8 869.954	-8.434	7.021	-6.330	-5.718	-2.217
(012)	9 000.140	9.214	-5.604	0.572	0.338	-0.255
(070)	10 086.045	-12.813	10.190	-8.091	-7.258	-2.738
(220)	10 284.369	7.921	-5.070	-0.519	-0.676	-0.720
(022)	10 521.762	8.880	-5.287	-0.245	-0.425	-0.713
(300)	10 599.687	13.675	-7.637	2.753	2.351	1.089
(102)	10 868.876	13.300	-8.554	2.000	1.591	0.466
(080)	11 253.997	-9.656	8.786	-7.216	-6.472	-2.413
(230)	11 767.388	7.463	-4.266	-1.163	-1.252	-0.948
(032)	12 007.776	8.423	-4.693	-0.988	-1.105	-1.068
(310)	12 139.316	13.297	-7.647	1.690	1.337	0.280
(112)	12 407.662	12.770	-8.404	0.992	0.641	-0.217
(090)	12 533.724	-4.257	5.320	-6.111	-5.573	-2.512
(400)	13 828.278	18.699	-9.178	4.553	4.023	2.032
(122)	13 910.881	12.684	-8.136	0.248	-0.058	-0.698
(202)	14 221.159	17.565	-10.845	3.025	2.490	1.006
(004)	14 537.504	18.781	-11.025	3.387	2.827	0.888
(330)	15 108.239	13.220	-6.327	0.806	0.559	-0.060
(410)	15 344.504	18.201	-9.181	3.383	2.906	1.072
(212)	15 742.803	17.176	-10.923	1.910	1.423	0.095
(420)	16 823.319	18.035	-1.437	2.912	2.490	0.874
(222)	17 227.380	16.977	-10.471	1.279	0.845	-0.306
(302)	17 458.214	22.467	-12.441	4.752	4.089	1.954
(104)	17 748.107	22.900	-12.934	4.625	3.946	1.745
(510)	18 892.778	23.185	-10.024	5.452	4.868	2.078
(600)	19 781.323	2.360	-10.422	-3.787	-3.269	-1.053
(610)	21 221.569	27.825	-10.398	7.691	7.010	3.556
(700)	22 529.288	34.197	-11.881	11.726	10.841	5.959
(001)	3 755.929	4.864	-2.835	0.800	0.658	0.201
(011)	5 331.267	4.595	-2.521	-0.052	-0.141	-0.245
(021)	6 871.520	4.175	-2.062	-0.876	-0.905	-0.628
(101)	7 249.819	9.322	-5.359	1.705	1.431	0.598
(031)	8 373.852	3.600	-1.336	-1.646	-1.605	-0.918
(111)	8 807.000	8.995	-5.222	0.740	0.517	-0.029
(041)	9 833.587	2.721	-0.303	-2.441	-2.315	-1.178
(121)	10 328.730	8.673	-4.827	-0.028	-0.196	-0.436
(201)	10 613.353	13.967	-7.483	2.978	2.573	1.227
(003)	11 032.405	14.073	-8.546	2.295	1.873	0.460
(131)	11 813.205	8.299	-4.083	-0.650	-0.754	-0.668
(211)	12 151.253	13.615	-7.494	1.931	1.574	0.433
(013)	12 565.006	14.231	-8.179	1.718	1.338	0.135
(221)	13 652.658	13.582	-7.073	1.390	1.080	0.144
(301)	13 830.937	18.738	1.953	4.585	4.056	2.051
(071)	13 835.373	-5.483	-4.762	-6.430	-5.826	-2.576
(023)	14 066.196	14.038	-7.996	0.956	0.622	-0.365

TABLE X. (Continued.)

(n_1, n_2, n_3)	Obs. ^a	V	CV	CVR	CVRQ	CVRQD
(103)	14 318.813	18.500	-10.541	3.596	3.049	1.239
(151)	14 647.977	6.067	-1.443	-2.274	-2.184	-1.231
(231)	15 119.031	13.403	-6.341	0.905	0.652	-0.056
(311)	15 347.958	18.481	-9.190	3.579	3.094	1.182
(033)	15 534.707	13.757	-7.539	0.280	0.000	-0.758
(113)	15 832.780	18.502	-10.395	2.823	2.317	0.641
(241)	16 546.319	12.972	-5.441	0.340	0.155	-0.308
(321)	16 821.634	19.612	-8.786	3.948	3.469	1.542
(401)	16 898.842	23.056	-10.175	6.110	5.487	2.744
(123)	17 312.551	18.389	-10.189	2.160	1.697	0.161
(203)	17 495.528	23.097	-12.147	5.206	4.536	2.178
(331)	18 265.821	19.259	-8.203	3.241	2.822	1.073
(411)	18 393.315	23.119	-9.965	5.420	4.839	2.064
(133)	18 758.633	18.362	-9.694	1.684	1.268	-0.144
(213)	18 989.960	22.975	-12.170	4.270	3.643	1.317
(341)	19 679.192	18.784	-7.377	2.609	2.257	0.645
(501)	19 781.103	28.677	-10.736	9.035	8.283	4.644
(421)	19 865.285	24.354	-9.629	5.725	5.152	2.090
(223)	20 442.777	23.555	-11.791	4.223	3.617	1.295
(303)	20 543.129	27.224	-13.176	6.836	6.076	3.028
(511)	21 221.827	27.776	-10.484	7.632	6.950	3.486
(431)	21 314.448	26.078	-9.127	6.496	5.922	2.446
(601)	22 529.440	34.162	-11.891	11.687	10.804	5.940
(701)	25 120.277	38.658	-13.142	13.700	12.742	6.459
$\sigma(81)$		16.41	7.96	4.29	3.87	1.85

^aReference 70.

VBOs are much more accurate than the higher energy ones. In fact, if one considers also the ZPE, the highest VBO present in Table X lies at an energy of about 30 000 cm⁻¹, which is higher than the expected range of stability of the CVQRD surface. This is also in line with Fig. 1, where we show four cuts through the difference between the CVQRD and the semiempirical surface of Ref. 66. The dotted lines show the cuts relative to energy above 25 000 cm⁻¹, and it is obvious that at those energies the CVQRD PES becomes quickly unreliable though the accuracy of the FIS3 PES in this region can also be questioned due to lack of relevant experimental data.

Another problem, of a different nature, is present at low energy. If one compares the pure bending VBOs ($0n_20$) with other VBOs of similar energy, it is easy to see that the former has a much greater discrepancy with the experimental values than the latter. This is also reflected in the cuts given in Fig. 1. The two top plots show the symmetric and antisymmetric stretches with a HOH angle equal to its equilibrium value, and the correspondence between the CVQRD and the semiempirical surfaces is almost perfect. The lower left plot shows the bending curve with the two OH bond lengths kept equal to their equilibrium values, while the lower right plot presents the stretching curve when the molecule is linear. In contrast to the previous cases, the differences between the *ab initio* CVQRD and the semiexperimental FIS3 surfaces are considerable. The symmetric bend shows the overshooting of the barrier to linearity discussed in a previous subsection, and presents a maximum deviation of several cm⁻¹. The linear symmetric stretch curve displays the largest discrepan-

cies between the CVQRD and the FIS3 semiempirical surface, which can be as large as 50 cm⁻¹. This large discrepancy is most likely due to shortcomings of the FIS3 PES. Nevertheless, the high bending VBOs must be particularly sensitive to this region of the PES and the underlying rearrangements in the electronic structure of water should partially explain the discrepancies reported in Table X.

VI. FUTURE IMPROVEMENTS

In our original study⁴ we identified a number of aspects of the computation of the CVQRD PESs which needed to be improved to achieve even higher accuracy. These included (a) increasing the number of grid points computed; (b) increasing the basis size from aug-cc-pV6Z used for the valence-only calculations and possibly doing all-electron computations, and (c) including a FCI correction to reach the limit in valence electron correlation.

The valence-only part of the CVQRD surfaces was determined at a grid of 346 points using low-energy points, i.e., those below 25 000 cm⁻¹, on a previously determined grid.³ Due to the limited range of grid points chosen originally for the CVQRD PES, it performed considerably worse in the region above 25 000 cm⁻¹. Therefore, in this continuation of the original study grid points in the high-energy region have been considered. Our strategy for selecting grid points for the new computations was initially to complete the rectilinear grid used in the original calculations, then to compute further points halfway between these grid points at low energies, and finally to perform extra calculations at points

TABLE XI. Term values for rotational levels with $J=20$ for four VBOs of H_2^{16}O obtained with the CVRQD PES. The differences, in cm^{-1} , are given as observed–calculated. The final column labeled +nBO contains results reflecting the effect of the full CVRQD surface supplemented with the rotational nonadiabatic corrections.

J	K_a	K_c	(n_1, n_2, n_3)	Obs. ^a	V	CV	CVR	CVRQ	CVRQD	+nBO
20	0	20	(000)	4 048.250	5.998	-1.698	-0.430	-0.492	-0.185	0.617
20	1	19	(000)	4 412.315	6.536	-1.822	-0.455	-0.523	-0.184	0.637
20	2	18	(000)	4 738.622	6.911	-1.860	-0.499	-0.566	-0.183	0.653
20	3	17	(000)	5 031.795	7.149	-1.828	-0.561	-0.625	-0.186	0.664
20	4	16	(000)	5 292.102	7.201	-1.681	-0.657	-0.709	-0.190	0.668
20	5	15	(000)	5 513.236	6.849	-1.246	-0.836	-0.861	-0.196	0.662
20	6	14	(000)	5 680.788	6.094	-0.553	-1.093	-1.076	-0.207	0.642
20	7	13	(000)	5 812.074	6.273	-0.612	-1.097	-1.082	-0.204	0.651
20	8	12	(000)	5 966.823	7.792	-1.675	-0.777	-0.824	-0.191	0.698
20	9	11	(000)	6 170.832	9.397	-2.765	-0.459	-0.569	-0.183	0.747
20	10	10	(000)	6 407.443	10.719	-3.627	-0.224	-0.383	-0.178	0.790
20	11	9	(000)	6 664.173	11.949	-4.421	-0.020	-0.225	-0.179	0.829
20	12	8	(000)	6 935.428	13.154	-5.198	0.171	-0.076	-0.183	0.867
20	13	7	(000)	7 217.562	14.337	-5.981	0.346	0.056	-0.200	0.896
20	14	6	(000)	7 507.545	15.490	-6.783	0.496	0.163	-0.242	0.905
20	15	5	(000)	7 802.709	16.700	-7.519	0.708	0.333	-0.219	0.980
20	16	4	(000)	8 100.291	17.860	-8.297	0.878	0.460	-0.240	1.017
20	17	3	(000)	8 397.648	19.012	-9.079	1.047	0.587	-0.265	1.054
20	18	2	(000)	8 691.927	20.157	-9.867	1.218	0.715	-0.292	1.093
20	19	1	(000)	8 979.881	21.299	-10.669	1.391	0.845	-0.324	1.132
20	20	0	(000)	9 257.459	22.450	-11.494	1.574	0.983	-0.360	1.174
20	0	20	(100)	7 627.587	10.067	-4.778	0.007	-0.191	-0.200	0.603
20	1	19	(100)	7 985.132	10.582	-4.898	-0.026	-0.228	-0.208	0.613
20	2	18	(100)	8 305.942	10.949	-4.924	-0.066	-0.268	-0.205	0.632
20	3	17	(100)	8 594.605	11.156	-4.908	-0.155	-0.353	-0.236	0.615
20	4	16	(100)	8 851.232	11.179	-4.764	-0.271	-0.457	-0.260	0.600
20	5	15	(100)	9 070.201	10.732	-4.509	-0.586	-0.747	-0.414	0.447
20	6	14	(100)	9 240.058	10.229	-3.737	-0.667	-0.790	-0.282	0.569
20	7	13	(100)	9 371.363	10.295	-3.697	-0.707	-0.826	-0.291	0.564
20	8	12	(100)	9 524.441	11.627	-4.572	-0.479	-0.647	-0.307	0.582
20	9	11	(100)	9 735.559	12.487	-5.081	-0.753	-0.937	-0.624	0.307
20	10	10	(100)	9 926.499	14.225	-5.567	-0.001	-0.264	-0.236	0.721
20	11	9	(100)	10 180.921	15.715	-7.256	0.403	0.076	-0.153	0.852
20	12	8	(100)	10 445.519	16.902	-8.100	0.605	0.231	-0.166	0.882
20	13	7	(100)	10 719.728	18.047	-8.898	0.779	0.362	-0.188	0.906
20	14	6	(100)	11 001.297	19.193	-9.670	0.958	0.499	-0.199	0.945
20	15	5	(100)	11 287.769	20.324	-10.439	1.129	0.628	-0.217	0.981
20	16	4	(100)	11 576.719	21.442	-11.211	1.294	0.752	-0.240	1.016
20	17	3	(100)	11 865.725	22.558	-11.979	1.464	0.879	-0.260	1.057
20	18	2	(100)	12 152.314	23.670	-12.750	1.635	1.008	-0.280	1.104
20	19	1	(100)	12 433.988	24.773	-13.531	1.803	1.134	-0.305	1.150
20	20	0	(100)	12 708.611	25.857	-14.323	1.960	1.249	-0.336	1.194
20	0	20	(010)	5 611.332	5.852	-1.356	-1.151	-1.164	-0.501	0.301
20	1	19	(010)	6 022.796	6.583	-1.567	-1.159	-1.181	-0.500	0.320
20	2	18	(010)	6 379.343	6.977	-1.614	-1.222	-1.244	-0.511	0.324
20	3	17	(010)	6 694.744	7.193	-1.556	-1.307	-1.324	-0.520	0.327
20	4	16	(010)	6 969.403	7.105	-1.302	-1.455	-1.454	-0.534	0.319
20	5	15	(010)	7 193.222	6.411	-0.631	-1.742	-1.698	-0.558	0.291
20	6	14	(010)	7 357.050	5.734	-0.028	-1.992	-1.909	-0.575	0.267
20	7	13	(010)	7 504.576	6.644	-0.633	-1.813	-1.765	-0.566	0.294
20	8	12	(010)	7 696.346	8.635	-1.989	-1.366	-1.399	-0.537	0.360
20	9	11	(010)	7 935.764	10.333	-3.105	-1.020	-1.119	-0.519	0.414
20	10	10	(010)	8 202.930	11.782	-4.019	-0.744	-0.896	-0.500	0.469
20	11	9	(010)	8 487.923	13.151	-4.876	-0.495	-0.696	-0.486	0.522
20	12	8	(010)	8 785.795	14.489	-5.711	-0.257	-0.506	-0.474	0.577
20	13	7	(010)	9 092.998	15.804	-6.532	-0.025	-0.321	-0.462	0.635
20	14	6	(010)	9 406.475	17.084	-7.136	0.188	-0.154	-0.462	0.683

TABLE XI. (Continued.)

J	K_a	K_c	(n_1, n_2, n_3)	Obs. ^a	V	CV	CVR	CVRQ	CVRQD	+nBO
20	15	5	(010)	9 723.513	18.378	-8.152	0.422	0.034	-0.446	0.754
20	16	4	(010)	10 041.365	19.630	-8.956	0.642	0.208	-0.441	0.816
20	17	3	(010)	10 357.333	20.888	-9.759	0.861	0.381	-0.439	0.878
20	18	2	(010)	10 668.500	22.123	-10.567	1.079	0.554	-0.443	0.941
20	19	1	(010)	10 971.505	23.349	-7.940	1.296	0.725	-0.456	0.999
20	20	0	(010)	11 262.092	24.592	-12.235	1.528	0.909	-0.472	1.062
20	0	20	(001)	7 740.685	10.669	-4.532	0.329	0.127	-0.038	0.765
20	1	19	(001)	8 095.899	13.469	-4.659	0.310	0.103	-0.035	0.787
20	2	18	(001)	8 414.969	11.571	-4.713	0.270	0.062	-0.038	0.800
20	3	17	(001)	8 702.378	11.828	-4.700	0.218	0.013	-0.040	0.812
20	4	16	(001)	8 958.979	11.935	-4.598	0.140	-0.057	-0.046	0.817
20	5	15	(001)	9 181.219	11.746	-4.283	0.003	-0.175	-0.052	0.813
20	6	14	(001)	9 357.724	11.142	-3.683	-0.219	-0.360	-0.057	0.801
20	7	13	(001)	9 470.982	11.113	-3.829	-0.420	-0.559	-0.193	0.674
20	8	12	(001)	9 615.124	12.112	-4.370	-0.103	-0.279	-0.083	0.805
20	9	11	(001)	9 800.338	13.660	-5.469	0.210	-0.029	-0.082	0.847
20	10	10	(001)	10 020.367	14.968	-6.342	0.457	0.167	-0.070	0.899
20	11	9	(001)	10 261.324	16.138	-7.134	0.650	0.317	-0.076	0.932
20	12	8	(001)	10 516.819	12.684	-7.897	0.293	0.113	-0.118	0.921
20	13	7	(001)	10 783.033	18.400	-8.666	1.000	0.583	-0.102	0.996
20	14	6	(001)	11 056.986	19.522	-9.420	1.173	0.715	-0.113	1.034
20	15	5	(001)	11 336.010	20.617	-10.167	1.326	0.827	-0.138	1.062
20	16	4	(001)	11 616.744	21.740	-9.618	1.514	0.974	-0.140	1.117
20	17	3	(001)	11 897.648	22.838	-11.693	1.680	1.098	-0.168	1.150
20	18	2	(001)	12 175.230	23.950	-4.474	1.870	1.246	-0.175	1.209
20	19	1	(001)	12 446.359	25.108	-13.145	2.114	1.448	-0.136	1.318
20	20	0	(001)	12 706.955	26.169	-13.966	2.265	1.556	-0.206	1.323
				$\sigma(164)$	15.36	7.02	1.00	0.79	0.31	0.81

^aReference 70.

where the surface appeared, by graphical inspection, to be poorly determined by the fit. Valence-only electronic energies are now available at a total of 1495 grid points at the QZ, 5Z, and 6Z ICMRCI+ Q levels; the data have been placed in the electronic archive.¹² The distribution of these points with energy is summarized in Table XII. Preliminary attempts to include the extra points in the fit proved the original CVRQD surface to be highly accurate. Since none of the correction surfaces are correct in the higher-energy region, there is only limited use of the extra points at present.

Although computer resources are still improving at a breathtaking speed, it is probably not useful to do valence-only aug-cc-pV7Z ICMRCI+ Q computations on water, partly due to the expected extrapolation difficulties. The more useful next step to be taken is to do all-electron calculations with a properly designed Gaussian basis and thus avoid separation of the valence and core electron correlation effects. Basis sets which include high exponents should also allow the utilization of the R12 approach of electronic structure theory and thus help in reaching the CBS limit in a more theoretically sound way.

To maintain the extreme accuracy of the CVRQD water surfaces at higher energies the proper inclusion of the FCI-MRCI energy difference is mandatory. Since this is not an easy task, it is left for future exploration how to deal with this problem the most efficient way. In light of the results

with the focal-point approach (FPA),³⁹ a smaller basis set might be sufficient to accurately recover this term but elaborate testing is needed.

Overall, for the lower-energy region of the ground-state PES of water we feel that the largest remaining source of error in the prediction of rovibrational levels is the Born-Oppenheimer surface, due to likely problems with basis set extrapolation, insufficient treatment of electron correlation, and separation of core and valence electrons. The correction surfaces should be reliable for this region, though reexamination of the DBOC surfaces might prove to be useful, especially since these surfaces are sensitive to the level of theory and the inclusion of diffuse basis functions during their calculation, see also Refs. 29, 52, 53, and 74.

It must also be stressed that the largest obstacle in the extension of the CVRQD surfaces to higher energies lies in the correction surfaces. These all have been designed to cover only the lower-energy region of the PES and thus to move beyond the 25 000 cm⁻¹ limit requires new approaches. For example, the relativistic correction surfaces will need to be recomputed using wave functions of multi-reference nature.

A final point which needs to be addressed is the accuracy of the numerical fitting of the various data points. This procedure adds an extra limitation to the total accuracy of the *ab initio* calculation. It is clear that the fitting error is rather

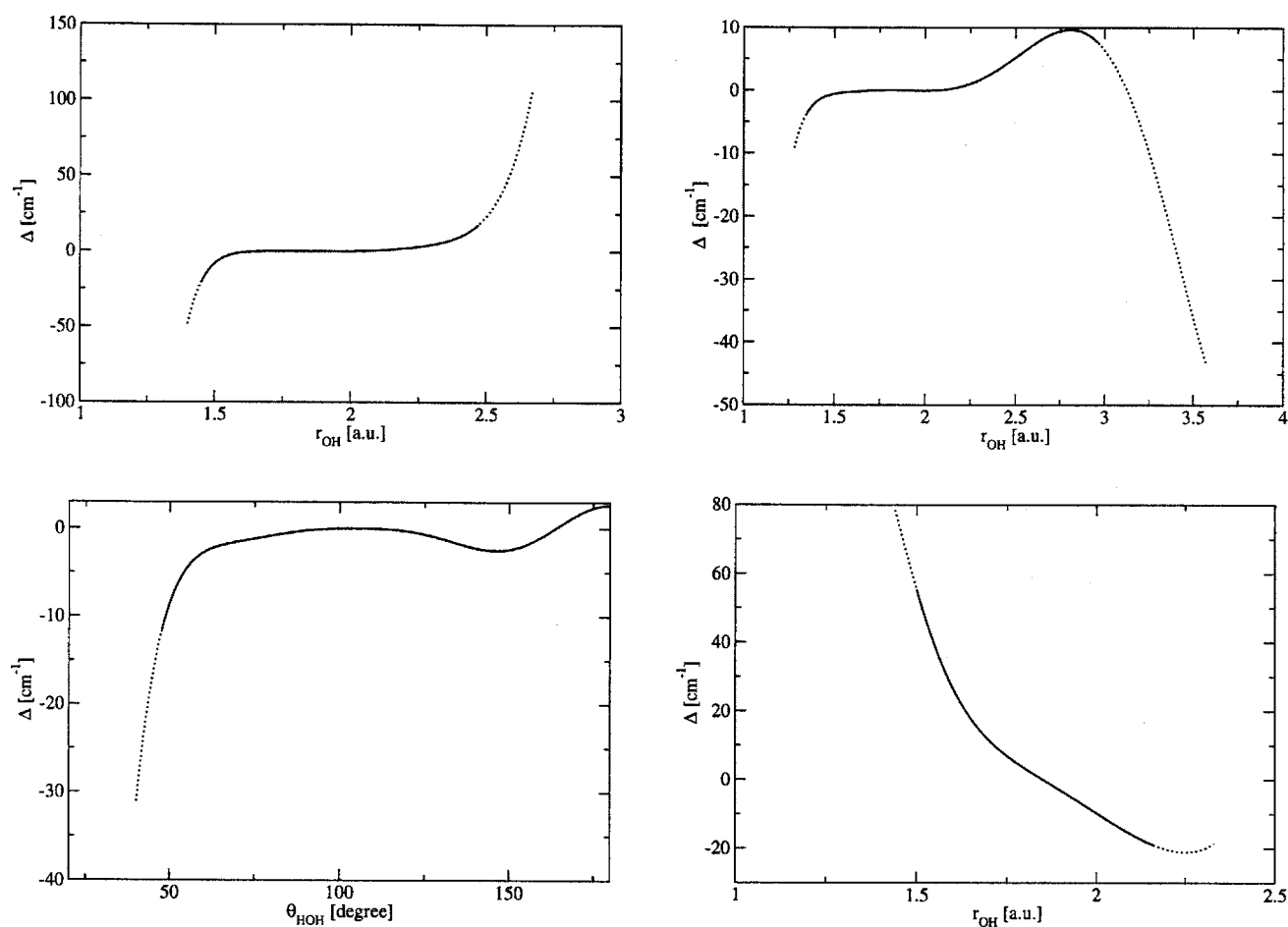


FIG. 1. Four profiles showing the difference Δ between the semiempirical FIS3 and the *ab initio* CVRQD surfaces. At the top left corner there is the cut relative to the symmetric stretch ($\theta = \theta_{eq}$), at the top right corner the asymmetric stretch ($\theta = \theta_{eq}$, $r_2 = r_{eq}$), at the bottom right corner the linear stretch ($\theta = 180.00$), finally at the bottom left corner there is the symmetric bend ($r_1 = r_2 = r_{eq}$). The full and dotted lines correspond to cutting the energy at 25 000 and 35 000 cm^{-1} , respectively.

small at the bottom of the surface, but increases significantly as one moves up in energy, due to the poor extrapolation quality of the polynomials which constitute the core of the fitted surface [term V_c in Eq. (8)]. The high number of polynomials needed to obtain a decent standard deviation (about 100 for this work) reflects the complexity of the surface in the middle- and low-energy parts. However, the direct consequence is that the surface behaves rather unpredictably out-

TABLE XII. The number of data points, N , in each energy interval, ΔE , computed as part of this study, and the fitting error of the CBS ICMRCI + Q surface in the different intervals. The number of coefficients optimized is 116.

ΔE (cm^{-1})	N	CVRQD
$\leq 5\,000$	103	0.33
5 000–10 000	99	1.09
10 000–15 000	135	1.91
15 000–20 000	170	2.58
20 000–25 000	195	3.51
25 000–30 000	177	
30 000–40 000	370	
$\geq 40\,000$	246	

side the original grid. This problem is particularly evident if one tries to fit a global surface, with points stretching up to dissociation. Obtaining a sufficiently accurate fit to the data points by including a sufficiently high number of polynomials is probably not possible. We think that a different functional form for the PES will have to be investigated in order to obtain a global representation of the water surface. As the complete CVRQD PESs are made of several such surfaces, it is easy to imagine that the problem is enhanced by their number. One possible solution would be to calculate all corrections on the same grid, and fit the CVRQD data just once. The downside of this approach is that one would then need to refit *ex novo* the PES whenever any of the corrections is reevaluated.

VII. CONCLUSIONS

We present a detailed analysis of the *ab initio* adiabatic CVRQD potential energy surfaces of the ground electronic state of water isotopologues originally presented in Ref. 4. These surfaces yield almost an order of magnitude improvement in predicted rotation-vibration energy levels as compared to the previous best *ab initio* surface.³ To achieve this

accuracy it has been necessary to both perform multireference configuration interaction calculations with very large basis sets, which must still be extrapolated, and to consider many effects usually neglected in *ab initio* studies: core correlation, electronic relativistic effects, quantum electrodynamics, and failure of the Born-Oppenheimer approximation.

Although equilibrium and vibrationally averaged (0 K) structures, harmonic and anharmonic force fields, zero-point energies, harmonic frequencies, and vibrational fundamentals characterizing our surfaces represent a significant advance, the rovibrational level predictions based on the CVRQD surfaces are usually still far less accurate than those that can be obtained from high-resolution spectra. To further improve on our surfaces would probably require the use of a different approach to the electron correlation problem: use of all-electron R12 MRCI computations plus consideration of remaining full CI effects.

Our CVRQD surfaces are only designed to cover the region probed by current high-resolution spectroscopic experiments. Nevertheless, the ultimate goal of theoretical rotation-vibration spectroscopy of water must be to model all water spectra, on the Sun, in the stars, in the atmosphere, in flames, and in the laboratory within a linewidth—or within the upper limit of the experimental accuracy—of 0.02 cm^{-1} or better. Extending the CVRQD surfaces to dissociation would be highly desirable but would require a number of issues to be addressed, particularly the calculations of the minor corrections using wave functions obtained from electron correlation treatments that dissociate reliably and accurately. Work in our laboratories is planned along these lines.

Finally, one byproduct of the large ICMRCI calculations presented here is an accurate estimate of the dipole moment of the water molecule at each geometry. We are currently using these calculations to determine a very high accuracy dipole moment function for the ground electronic state of water;⁷⁵ this surface will also include corrections for “minor” effects such as correlation of the oxygen *1s* electrons and the relativistic motion of the electrons.

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- ¹G. S. Kedziora and I. Shavitt, *J. Chem. Phys.* **109**, 5547 (1997).
- ²A. G. Császár and I. M. Mills, *Spectrochim. Acta, Part A* **53**, 1101 (1997).
- ³H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997).
- ⁴O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles, *Science* **299**, 539 (2003).
- ⁵M. G. Bucknell and N. C. Handy, *Mol. Mater.* **28**, 777 (1974).
- ⁶R. J. Bartlett, I. Shavitt, and G. D. Purvis, *J. Chem. Phys.* **71**, 281 (1979).
- ⁷P. J. Knowles, G. J. Sexton, and N. C. Handy, *Chem. Phys.* **72**, 337 (1982).
- ⁸J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **96**, 7633 (1992).
- ⁹G. Czako, T. Furtenbacher, A. G. Császár, and V. Szalay, *Mol. Phys.* **102**, 2411 (2004).
- ¹⁰J. Tennyson, P. Barletta, M. A. Kostin, O. L. Polyansky, and N. F. Zobov, *Spectrochim. Acta, Part A* **58**, 663 (2002).
- ¹¹A. G. Császár, G. Czako, T. Furtenbacher, J. Tennyson, V. Szalay, S. V. Shirin, N. F. Zobov, and O. L. Polyansky, *J. Chem. Phys.* **122**, 214305 (2005).
- ¹²See EPAPS Document No. E-JCPA6-125-303643 for electron versions of all the potential energy surfaces as FORTRAN programs. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- ¹³T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ¹⁴The (aug-)cc-pVnZ basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830.
- ¹⁵H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- ¹⁶S. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).
- ¹⁷H.-J. Werner and P. J. Knowles, MOLPRO (version 2002.1) is a package of *ab initio* electronic structure programs.
- ¹⁸R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988).
- ¹⁹A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, *Chem. Phys. Lett.* **293**, 317 (1998); **312**, 613(E) (1999).
- ²⁰H. M. Quiney, P. Barletta, G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson, *Chem. Phys. Lett.* **344**, 413 (2001).
- ²¹J. F. Stanton, J. Gauss, J. D. Watts *et al.*, ACESII Mainz-Austin-Budapest version; MOLEUCLE (J. Almlöf and P. R. Taylor); PROPS (P. R. Taylor); ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, and J. Olsen).
- ²²DALTON, a molecular electronic structure program, Release 2.0 (2005); see <http://www.kjemi.uio.no/software/dalton/dalton.html>
- ²³I. P. Grant and H. M. Quiney, *Int. J. Quantum Chem.* **80**, 283 (2000).
- ²⁴P. Pyykkö, K. G. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A* **63**, 024502 (2001).
- ²⁵M. Kállay and P. R. Surján, *J. Chem. Phys.* **115**, 2945 (2001).
- ²⁶For the current version of the program, see <http://www.mrcc.hu>
- ²⁷K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- ²⁸H. Lischka, R. Shepard, I. Shavitt *et al.*, CCLUMBUS, an *ab initio* electronic structure program, Release 5.9.1 (2006).
- ²⁹E. F. Valeev and C. D. Sherrill, *J. Chem. Phys.* **118**, 3921 (2003).
- ³⁰T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, PSI3 (version 3.2) is a package of *ab initio* electronic structure programs.
- ³¹C. D. Sherrill and H. F. SchaeferIII, *Adv. Quantum Chem.* **34**, 143 (1999).
- ³²J. Olsen, *Chem. Phys. Lett.* **169**, 463 (1990).
- ³³J. Olsen, *J. Chem. Phys.* **89**, 2185 (1988).
- ³⁴M. Kállay, P. G. Szalay, and P. R. Surján, *J. Chem. Phys.* **117**, 980 (2002).

- ³⁵ A. G. Császár, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III, in *Computational Molecular Spectroscopy*, edited by P. Jensen and P. R. Bunker (Wiley, Chichester, 2000), pp. 15–68.
- ³⁶ P. G. Szalay and R. J. Bartlett, *Chem. Phys. Lett.* **214**, 481 (1993).
- ³⁷ T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- ³⁸ W. Klopper, K. L. Bak, P. Jorgensen, J. Olsen, and T. Helgaker, *J. Phys. B* **32**, R103 (1999).
- ³⁹ A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108**, 9751 (1998).
- ⁴⁰ E. F. Valeev, W. D. Allen, H. F. Schaefer III, and A. G. Császár, *J. Chem. Phys.* **114**, 2875 (2001).
- ⁴¹ D. Feller, *J. Chem. Phys.* **98**, 7059 (1993).
- ⁴² T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ⁴³ A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, and J. Olsen, *Chem. Phys. Lett.* **302**, 437 (1999).
- ⁴⁴ M. Kállay, J. Gauss, and P. G. Szalay, *J. Chem. Phys.* **119**, 2991 (2004).
- ⁴⁵ M. Kállay and J. Gauss, *J. Chem. Phys.* **120**, 6841 (2004).
- ⁴⁶ Our tests included basis sets up to aug-cc-pV6Z, significantly larger than those used in Ref. 3.
- ⁴⁷ R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
- ⁴⁸ P. Pyykkö, *Adv. Quantum Chem.* **11**, 353 (1978).
- ⁴⁹ G. Tarczay, A. G. Császár, W. Klopper, and H. M. Quiney, *Mol. Phys.* **99**, 1768 (2001).
- ⁵⁰ H. M. Quiney, H. Skanne, and I. P. Grant, *Chem. Phys. Lett.* **290**, 473 (1998).
- ⁵¹ P. R. Bunker and R. E. Moss, *J. Mol. Spectrosc.* **80**, 217 (1980).
- ⁵² D. W. Schwenke, *J. Chem. Phys.* **118**, 6898 (2003).
- ⁵³ D. W. Schwenke, *J. Phys. Chem. A* **105**, 2352 (2001).
- ⁵⁴ I. N. Kozin, M. M. Law, J. Tennyson, and J. M. Hutson, *Comput. Phys. Commun.* **163**, 85 (2004).
- ⁵⁵ R. J. Barber, J. Tennyson, G. J. Harris, and R. N. Tolchenov, *Mon. Not. R. Astron. Soc.* **368**, 1087 (2006).
- ⁵⁶ D. W. Schwenke, *J. Phys. Chem.* **100**, 2867 (1996); **100**, 18884(E) (1996).
- ⁵⁷ T. Furtenbacher, G. Czakó, B. T. Sutcliffe, A. G. Császár, and V. Szalay, *J. Mol. Struct.* **780–781**, 283 (2006).
- ⁵⁸ G. Czakó, T. Furtenbacher, and A. G. Császár, (unpublished).
- ⁵⁹ S. Carter and N. C. Handy, *J. Chem. Phys.* **87**, 4294 (1987).
- ⁶⁰ P. Jensen, *J. Mol. Spectrosc.* **133**, 438 (1989).
- ⁶¹ O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **105**, 6490 (1996).
- ⁶² R. Lanquetin, L. H. Coudert, and C. Camy-Peyret, *J. Mol. Spectrosc.* **195**, 54 (1999).
- ⁶³ J. S. Kain, O. L. Polyansky, and J. Tennyson, *Chem. Phys. Lett.* **317**, 365 (2000).
- ⁶⁴ G. Tarczay, A. G. Császár, W. Klopper, V. Szalay, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **110**, 11971 (1999).
- ⁶⁵ N. F. Zobov, S. V. Shirin, O. L. Polyansky, J. Tennyson, P.-F. Coheur, P. F. Bernath, M. Canleer, and R. Colin, *Chem. Phys. Lett.* **414**, 193 (2005).
- ⁶⁶ S. V. Shirin, O. L. Polyansky, N. F. Zobov, R. I. Ovsyannikov, A. G. Császár, and J. Tennyson, *J. Mol. Spectrosc.* **236**, 216 (2006).
- ⁶⁷ P.-F. Coheur, P. F. Bernath, M. Canleer, R. Colin, O. L. Polyansky, N. F. Zobov, S. V. Shirin, R. J. Barber, and J. Tennyson, *J. Chem. Phys.* **122**, 074307 (2005).
- ⁶⁸ M. Abramovitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).
- ⁶⁹ A. G. Császár, in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1997), pp. 13–30.
- ⁷⁰ J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, and P. F. Bernath, *J. Phys. Chem. Ref. Data* **30**, 735 (2001).
- ⁷¹ R. A. Toth, *J. Opt. Soc. Am. B* **9**, 462 (1992).
- ⁷² S. N. Mikhailenko, V. G. Tyuterev, and G. Mellau, *J. Mol. Spectrosc.* **217**, 195 (2003).
- ⁷³ R. A. Toth, *J. Mol. Spectrosc.* **162**, 41 (1993).
- ⁷⁴ N. F. Zobov, O. L. Polyansky, C. R. Le Sueun, and J. Tennyson, *Commun. Pure Appl. Math.* **260**, 381 (1996).
- ⁷⁵ A. E. Lynas-Gray, L. Lodi, R. N. Tolchenov *et al.* (unpublished).