A new *ab initio* ground-state dipole moment surface for the water molecule

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A valence-only (V) dipole moment surface (DMS) has been computed for water at the internally contracted multireference configuration interaction level using the extended atom-centered correlation-consistent Gaussian basis set aug-cc-pV6Z. Small corrections to these dipole values, resulting from core correlation (C) and relativistic (R) effects, have also been computed and added to the V surface. The resulting DMS surface is hence called CVR. Interestingly, the C and R corrections cancel out each other almost completely over the whole grid of points investigated. The ground-state CVR dipole of $H_2{}^{16}O$ is 1.8676 D. This value compares well with the best *ab initio* one determined in this study, 1.8539 ± 0.0013 D, which in turn agrees well with the measured ground-state dipole moment of water, 1.8546(6) D. Line intensities computed with the help of the CVR DMS shows that the present DMS is highly similar to though slightly more accurate than the best previous DMS of water determined by Schwenke and Partridge [J. Chem. Phys. **113**, 16 (2000)]. The influence of the precision of the rovibrational wave functions computed using different potential energy surfaces (PESs) has been investigated and proved to be small, due mostly to the small discrepancies between the best *ab initio* and empirical PESs of water. Several different measures to test the DMS of water are advanced. The seemingly most sensitive measure is the comparison between the *ab initio* line intensities and those measured by ultralong pathlength methods which are sensitive to very weak transitions. © *2008 American Institute of Physics.*
[DOI: 10.1063/1.2817606]

I. INTRODUCTION

The rotation-vibration spectrum of water is arguably the single most important spectrum of any species. Water dominates both the incoming and outgoing ("greenhouse") absorption of radiation in the earth's atmosphere,[1] is a major product of most combustion processes and is thus used to follow their evolution,[2] and is important in a whole variety of astrophysical environments.[3] Due to a dedicated and concerted effort of many researchers, positions (frequencies) of many water transitions are known with high accuracy, typically better than 10^{-3} cm^{-1}.[4,5] On the other hand, there remains much uncertainty, and indeed dispute, about the strength (e.g., Ref. 6) and line-shape (e.g., Ref. 7) of these transitions. It is the purpose of this paper to address issues related to the line strengths of $H_2{}^{16}O$.

Accurate measurement of the intensities of the rotational-vibrational transitions of water in the laboratory is technically demanding even at room temperature and there appears to be no available data on absolute intensities for high temperature water, despite their importance in many applications.[8] This state of affairs places considerable emphasis on theory to produce reliable procedures for calculating accurate transition intensities.

The calculation of reliable rotational-vibrational and purely rotational transition intensities relies on knowledge of the nuclear motion wave functions of the upper and lower states involved and of the dipole moment surface (DMS) (note that in general the dipole of water is a vector with two nonzero components). Considerable emphasis has been placed on obtaining high-accuracy rotation-vibration wave functions for the major isotopologues of water through accu-

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rate variational computations,[9–15] but traditionally rather less emphasis has been devoted to obtaining high-accuracy DMSs.

For potential energy surfaces (PES), which determine the rotational-vibrational wave functions, experience has shown that it is still necessary to tune them using experimental data if one wants to obtain transition frequencies starting to approach experimental accuracies,[11,12,14,16] which may loosely be defined as 0.02 cm^{-1} on average. Tests have shown that although it is in principle possible to tune DMSs to experimental data,[10] this gives poorer results than purely *ab initio* procedures for determining the DMS.[17] In part this is due to experimental uncertainties which are much larger for transition intensities than for line positions. This situation persists despite the recent advances in high precision experiments.[7,18,19]

Despite the benchmark nature of the problem there are relatively few *ab initio* DMSs available for the water molecule. Notable examples are given in Refs. [11] and [20–23]. The most accurate *ab initio* dipole data available is due to Partridge and Schwenke,[11] who subsequently found it necessary to perform a systematic refit of their data[23] giving a surface, denoted here as SP2000, which gives very good transition intensities over a wide range of frequencies.[24,25]

Ab initio studies of the ground-state PES of water,[13,15,26] and indeed of other molecules,[27–30] have shown the importance of including corrections[31–33] to standard *ab initio* procedures in the form of core-core and core-valence corrections,[11,13] first-order[34] and higher-order relativistic corrections,[35] adjustments due to the limited precision of the Born-Oppenheimer approximation[26,36,37] and even quantum electrodynamic effects.[38] So far none of these corrections have been considered for the DMS of water.

In this paper we present a new *ab initio* determination of the water DMS performed with a high-level treatment of valence electron correlation and a large basis set. The underlying electronic structure calculations produced the valence part of the very accurate CVRQD PESs of the isotopologues of water.[13,15] We consider the effects of the two largest corrections to the valence-only solution resulting in a DMS: the core and electron relativistic corrections. Taken individually each of these corrections gives a small but apparent effect but, as it emerged in the present case, they cancel each other out to a large extent so that their overall effect is negligible at the level of precision we are investigating. Our final DMS, called CVR as it includes core (C) and relativistic (R) corrections to the valence-only (V) surface, is tested against both a variety of measurements and the previous-best DMS from Ref. [23]. The CVR DMS is made available via EPAPS.[39]

II. ELECTRONIC STRUCTURE COMPUTATIONS

Similarly to recent *ab initio* determinations of the PESs of water,[13,15] the high-level valence-only dipole moment computations of this study, performed at the aug-cc-pV6Z IC-MRCI level and resulting in the basic part of the DMS of this paper, have been complemented with appropriate core

and relativistic corrections. We discuss each of these surfaces in the following subsections.

A. Valence-only computations

The dipole moment calculations were performed at a series of 1497 geometries.[15] A file listing these structures and the corresponding dipole moment components calculated with the aug-cc-pV6Z basis are given in EPAPS.[39] Most of these results are side products of the extensive computations performed for computing the CVRQD PES (Refs. [13] and [15]) but approximately 50 points were added to cover regions where graphical inspection of our fits suggested that the dipole moment components were particularly poorly determined. As discussed below, not all the dipole data computed were used in our final fit. As to details, the internally contracted multireference configuration interaction (IC-MRCI) calculations were performed using a series of augmented correlation-consistent aug-cc-pVnZ (Refs. [40] and [41]) basis sets with $n=4$, 5, and 6 and the same eight-electrons-eight-orbitals (8 by 8) complete active space (CAS) as used in Ref. [13].

Dipole moments were calculated as expectation values (XP) and not energy derivatives (ED) from the IC-MRCI wave functions, as implemented in the software MOLPRO.[42] A rather extensive analysis of the main sources of possible error in these nonrelativistic dipole moment calculations was carried out. For these tests, dipole moments were computed for a set of 14 geometries, given in Table V, in order to investigate the effect of (i) basis set size, (ii) method of computation of the dipole (XP versus ED), and (iii) electronic correlation treatment. All these calculations were done correlating all the electrons with the aug-cc-pCVnZ ($n=3-6$) basis sets using MOLPRO. The energy-derivative values were obtained with the two-point formula $E'(0)=[E(\lambda) -E(-\lambda)]/(2\lambda)$ with $\lambda=0.00075$, where λ is the electric field strength. For the IC-MRCI values three reference spaces were used, one is the 8 by 8 CAS (but with core electrons correlated, as well), denoted CAS1 in Table V and two larger CASs with one and two further unoccupied a_1 orbitals included in the active space, denoted CAS2 and CAS3, respectively. As the amount of data generated is extensive, only some results are reported for the equilibrium geometry in Table I and we only quote the conclusions we drew from the analysis of the other points. The use of diffuse functions, as implied by the augmentation (aug) of the basis, is generally held to be of particular importance for calculating accurate dipoles.

As to extension of the atom-centered Gaussian basis, both the ED and the XP dipoles vary typically by 4×10^{-3}, 1.5×10^{-3}, and 0.5×10^{-3} a.u. when increasing the cardinal number (n) of the basis by 1, from 3Z$\rightarrow$4Z, 4Z$\rightarrow$5Z, and 5Z$\rightarrow$6Z, respectively. This convergence pattern indicates that the basis set error is only a few times 10^{-4} a.u. for the aug-cc-pV6Z dipoles computed for the CVR DMS. It was our original intention to explore the idea of extrapolating the dipole calculations to give an estimate of the complete basis set (CBS) limit dipole at each geometry. However, inspection of the calculations suggested that in fact the dipoles were

TABLE I. *Ab initio* all-electron equilibrium dipole moments, in a.u., of water, computed at different coupled-cluster levels of theory at the equilibrium Born-Oppenheimer reference structure of $r_e^{BO}=0.95782$ Å and $\alpha_e^{BO}=104.485°$. (ED=energy derivative and XP=expectation value. See text for a description of the complete active spaces CAS1, CAS2, and CAS3.)

Level	Method	aug-cc-pCVDZ	aug-cc-pCVTZ	aug-cc-pCVQZ	aug-cc-pCV5Z	aug-cc-pCV6Z
HF	ED	0.78721	0.77996	0.77944	0.77951	0.77952
CCSD	ED	0.73550	0.73408	0.73799	0.73939	0.73995
CCSD(T)	ED	0.72761	0.72513	0.72894	0.73037	0.73091
CCSDT	ED	0.72720	0.72502			
CCSDTQ	ED	0.72664				
IC-MRCI,CAS1	XP	0.73363	0.73233	0.73611	0.73756	0.73811
IC-MRCI,CAS2	XP	0.73161	0.72941	0.73293	0.73430	0.73482
IC-MRCI,CAS3	XP	0.73041	0.72790	0.73135	0.73269	0.73320
IC-MRCI+Q,CAS1	ED	0.72670	0.72430	0.72821	0.72963	0.73018
IC-MRCI+Q,CAS2	ED	0.72661	0.72393	0.72778	0.72921	0.72975
IC-MRCI+Q,CAS3	ED	0.72665	0.72400	0.72783	0.72925	0.72980

converged with respect to increases in the basis set size to better than 5×10^{-4} a.u. with the aug-cc-pV6Z basis set and the idea of extrapolation was not pursued. While it is known[43] that the correlation-consistent (cc) basis sets perform best at or near usual stationary points, and less well half way in between a minimum and a corresponding dissociation asymptote, for example, the small related errors cannot be checked easily for the PES of water and it is impossible to follow them for the DMS. The relatively fast convergence of the dipoles can be rationalized by noting that they are, by definition, expectation values of a one-electron operator and these usually show improved convergence characteristics with respect to atom-centered Gaussian basis sets.

There is extensive discussion in the literature, see, for example, Refs. 44–48, concerning the most appropriate way of calculating first-order properties, such as dipole moments, for approximate solutions of the electronic Schrödinger equation. Dipole moments can be calculated in two ways: (i) as the expectation value of the dipole vector $\boldsymbol{\mu}$, and (ii) as the derivative of the energy $E(\lambda)$ for $\lambda=0$ of the perturbed Hamiltonian $\hat{H}'=\hat{H}+\lambda\boldsymbol{\mu}$, where λ is the external perturbation. For many types of approximate wave functions, such as MRCI, in which not all relevant variational parameters have been optimized, the two methods do not yield the same value. There have been several arguments suggesting that in these cases the energy-derivative values should be more accurate.[49,50] Changing the method of computation from XP to ED results in differences of about 5, 4, and 3×10^{-3} a.u. for the smallest, middle, and largest CAS investigated. This is thus probably the major source of remaining error in our dipole computations. ED values seem to be more accurate than XP ones and they are in much closer agreement with the coupled clusters with singles, doubles, triples, and quartets (CCSDTQ) equilibrium value computed with the aug-cc-pCVDZ basis set and with the code ACES II (Ref. 51) and MRCC.[52] ED values are also more stable with respect to increase in the CAS size, especially if one uses Davidson- or Pople-corrected energies instead of the plain MRCI ones. Going from the smallest to the biggest CAS results (for all basis sets) in a change of about 7×10^{-4} a.u. for the ED values and of about 5×10^{-3} a.u. for the XP ones. The close agreement between our valence-only DMS and that of

Schwenke and Partridge (SP2000) (Ref. 23) lends further support to the observation made above since the SP2000 surface is based on an IC-MRCI calculation performed with the cc-pV5Z basis from which some functions were deleted. The two sets of dipole moment computations were based on the same active space and both used the same expectation value technique built into MOLPRO. A larger CAS or a calculation procedure for the dipole as an energy derivative could partially spoil the agreement with SP2000.

B. Core corrections

The core correction computations are designed to augment the valence-only calculations and result in full ten-electron Born-Oppenheimer estimates of the dipole moments of water at each grid point. The core correction surface computations utilized the size-consistent coupled cluster (CC) method with singles and doubles and a partial treatment of triples [CCSD(T)],[53] as size consistency is a basic requirement when differences in computed results referring to different number of electrons are taken. The frozen-core and all-electron CCSD(T) dipole moment calculations utilized as a basis the simple atom-centered Gaussian functions of the uncontracted aug-cc-pCVTZ and aug-cc-pVTZ basis of O and H, respectively.[40,54] The calculations have been performed over a grid containing 364 points and employed the program package ACES II.[51] Since ACES II always reorients the molecular frame and performs the electronic structure calculations in the principal axes frame, special attention was paid for structures of C_s point-group symmetry to reorient the core dipole corrections in order to make them consistent with the valence-only ones of MOLPRO. A file listing the 364 structures and the corresponding core corrections to the dipole moment components are given in EPAPS.[39] This surface was fitted separately from the valence-only surface, see below.

C. Relativistic effects

The relativistic effect on dipole moments is defined as the difference between relativistic and nonrelativistic values obtained at a given grid point. Several tests were carried out to investigate the level of theory necessary to obtain a given

TABLE II. Structures used for tests of the relativistic contributions to the dipole moment surface of water. Bond lengths (r) are in Å and bond angle (θ) is in degrees. The reported energies (in cm^{-1}) are those given by the CVRQD surface of H$_2$ ^{16}O (Refs. 13 and 15).

Structure	θ	r_1	r_2	Energy
Equilibrium	104.52	0.9576	0.9576	0.2
Near linear	170	0.80	1.00	18166.5
Bond compressed	100	0.75	0.95	16022.0
Bond stretched	100	0.95	1.00	417.6

precision. Several levels of approximation were tested: (i) full Dirac-Coulomb, (ii) spin-free Dirac-Coulomb, (iii) second-order scalar-relativistic Douglas-Kroll-Hess theory (DKH2) (see Ref. 55 for a recent review), and (iv) mass-velocity+one-electron Darwin operator (MVD1) treated perturbatively.[56] The final correction surface uses points calculated with (ii) but we show that the simpler approach (iv) would have also achieved a similar accuracy.

1. Dirac-Coulomb calculations

Relativistic values for the dipole of water were calculated in the four-component formulation as implemented in the program DIRAC (Ref. 57) and employed a nucleus that is modeled by a Gaussian charge distribution.[58] The nonrelativistic calculations to be subtracted from the relativistic ones to get the net relativistic effect were performed with DIRAC as well and are based on the Lévy-Leblond reformulation of the Schrödinger equation.[59] The method used for the calculation of the relativistic effect on the DMS of water was tested at four structures each of which probe a different region of the DMS (see Table II).

The test calculations were performed at the HF, MP2, CCSD, and CCSD(T) levels of theory with all electrons correlated. At the HF level the dipole moment was calculated as an expectation value. The correlation contribution to the dipole moment was calculated using the energy-derivative method with perturbation strength of $\lambda = \pm 2.0 \times 10^{-4}$. This contribution was added to the HF expectation value.

To isolate the effect of spin-orbit coupling (SOC) on the dipole moment of water we have compared calculations using the full Dirac-Coulomb (DC) Hamiltonian with calculations based on the spin-free formalism of Dyall.[60] These calculations were performed at the HF level using the aug-cc-pVDZ basis of Kendall *et al.*[41] in an uncontracted form. The results are reported in Table III and show that the inclusion

TABLE III. Effect of spin-orbit coupling on the magnitude of the dipole moment in a.u., computed at the four reference structures of Table II. SFDC are the Dirac-Coulomb spin-free calculations, SOC are the calculations including spin-orbit coupling, and SOC-effect indicates the net effect of spin-orbit coupling.

Structure	SFDC	SOC	SOC-effect
Equilibrium	0.785038	0.785036	−0.000002
Near linear	0.255316	0.255314	−0.000001
Bond compressed	0.780764	0.780763	−0.000002
Bond stretched	0.989326	0.819323	−0.000002

of spin-orbit interaction results for all four test geometries in a minuscule shrinkage of the dipole magnitude of about 2×10^{-6} a.u. and can thus be neglected. Inclusion of SOC in the correlated relativistic calculations makes the computations considerably more demanding but does not increase the computational cost at the HF level much. We thus did include the SOC correction at the HF level.

For efficiency reasons we furthermore neglected contributions from the so-called (SS|SS) part of the Coulomb repulsion operator and from the Gaunt interaction. Calculations with and without inclusion of the (SS|SS) type of two-electron integrals indicate that the contribution of this type of integrals is negligible for the dipole moment of water (below 10^{-7} a.u.). The Gaunt (SL|SL) type integrals come in at order α^2 which is two orders lower than the (SS|SS) integrals that contribute only at order α^4. However, the fact that spin-orbit effects are small does indicate that also the spin-other-orbit effects (to which the Gaunt or Breit interaction amounts in a two-component picture) will be small.

Four different basis sets from the correlation consistent family of basis sets were tested, aug-cc-pVTZ,[41] aug-cc-pVQZ,[41] aug-cc-pCVTZ, and aug-cc-pCVQZ.[61] These were all decontracted because the standard contraction coefficients are determined using nonrelativistic methods and thus are not suitable for our purpose. For the oxygen atom a minor complication arises in decontracting the aug-cc-pCVnZ sets because the additional tight exponents lie close to other exponents. We resolved this by dropping for the aug-cc-pCVTZ set the two tight s exponents and replacing them individually by exponents that lie in between existing exponents using an even-tempered scheme $\alpha_b = \sqrt{\alpha_a \alpha_c}$, where α_a and α_c are the existing (aug-cc-pVnZ) exponents and α_b is the new tight exponent. For example, the tight s exponent 7.845 from the aug-cc-pCVTZ set has been replaced by 10.199 which is obtained by applying the above formula to the exponents 16.760 and 6.207. The same idea was applied to the three extra s exponents from the aug-cc-pCVQZ set and to two of the three extra p exponents from the same aug-cc-pCVQZ basis. All other extra tight exponents are well separated from others and could be included in the calculations without modification.

The results show, for all four geometries, a very weak dependence on basis set size so that accurate values can be obtained even with the smaller basis sets. Going from the smallest aug-cc-pVTZ to the largest aug-cc-pCVQZ basis results in a change in the magnitude of the dipole of only about 2×10^{-5} a.u.; this value is halved going from aug-cc-pCVTZ to aug-cc-pCVQZ. We then decided to perform the correlated calculations using the aug-cc-pCVTZ basis. Anyway, as the HF calculations are relatively fast we have calculated the HF contribution to the relativistic effect on the dipole moment using the aug-cc-pCVQZ basis set.

In the complete set of structures used to calculate the DMS of water there were three structures that appeared to be particularly problematic for the CCSD(T) method. These structures have $\theta = 104.52°$ and $r_1 = 0.95$ Å, while r_2 is 3.0, 5.0, and 7.0 Å. These structures, for which the wave function is not well described by a single determinant, have been treated separately using the complete active space self-

TABLE IV. Test of different methods of computation of the relativistic effects on the dipole moment. All values are calculated with the aug-cc-pCVTZ basis set uncontracted as described in the text. Given (in a.u.) is the net relativistic effect on the magnitude of the dipole, $|\nu|_{rel}-|\mu|_{nonrel}$. SFDC, spin-free Dirac-Coulomb with neglect of (SS··SS) integrals. MVD1, perturbative treatment of the mass-velocity+one-electron Darwin term, ACPF method for electron correlation, CAS=smaller, dipoles computed by energy derivatives. DKH2, second order scalar-relativistic Douglas-Kroll-Hess theory, ACPF method for electron correlation, dipoles computed as expectation values.

Geometry	SFDC				MVD1	DKH2
	aug-cc-pVTZ	aug-cc-pCVTZ	aug-cc-pVQZ	aug-cc-pCVQZ	aug-cc-pCVTZ	
Equilibrium	−0.001720	−0.001710	−0.001703	−0.001697	−0.001627	−0.001613
Near linear	−0.000150	−0.000149	−0.000148	−0.000147	−0.000151	−0.000149
Bond compressed	−0.001419	−0.001411	−0.001405	−0.001400	−0.001300	−0.001288
Bond stretched	−0.001824	−0.001813	−0.001807	−0.001801	−0.001725	−0.001711

consistent-field (CASSCF) method. The CASSCF calculations are performed in C_s symmetry with the same active space as used by Partridge and Schwenke,[11] six a' and two a'' orbitals and eight electrons active using the aug-cc-pCVQZ basis with the DALTON electronic structure program.[62] Comparison of the nonrelativistic CCSD(T) values with nonrelativistic MRCI values for the other geometries of the set confirmed that CCSD(T) should be an adequate method to calculate the relativistic effect for the other 361 points. Data for individual geometries have been placed in EPAPS.[39]

2. Approximate calculation of the relativistic corrections

Relativistic effects were also investigated at simpler levels of theory using MOLPRO. MOLPRO can calculate the expectation value of the MVD1 operator (i.e., the one-electron relativistic correction) on the wavefunctions of the perturbed system $\hat{H}+\lambda\boldsymbol{\mu}$; the derivative of this energy correction with respect to λ for $\lambda=0$ gives the relativistic correction to the dipole. The computation of the expectation value of the MVD1 operator adds virtually no time to a standard nonrelativistic computation.

With MOLPRO one can also perform calculations within the second-order scalar-relativistic Douglas-Kroll-Hess (DKH2) theory.[55] In this approach relativistic effects are included in an approximate way at the onset by a modification of the Schrödinger equation and the given values for energies and dipoles are already corrected for relativity. If one desires to obtain only the net effect, it is necessary to perform a standard nonrelativistic calculation and then take the difference of the two results. A DKH2 calculation can be combined with any electronic structure method and the increase in the amount of computations with respect to a standard one is negligible. We have performed the same convergence tests as done for the Dirac-Coulomb calculations for the same set of four geometries and the same basis sets. Electron correlation has been treated with CCSD, CASSCF (CAS1 as above), MRCI, ACPF, AQCC, and RSPT2. Some results are shown in Table IV.

The main conclusions from the MVD1 and DKH2 calculations are as follows. With respect to Dirac-Coulomb calculations, the MVD1 and DKH2 deviations are on the order of 10^{-4} a.u. MVD1 and DKH2 agree very well with each other, down to $1-5\times10^{-5}$ a.u.. This small discrepancy could

partly be due to a picture change error[63] that is known to be small for valence properties of light elements and was not included. This difference is anyway at the level where numerical noise may become important. Similarly to what was noticed for the Dirac-Coulomb calculations, the effect of basis set size increase is very small, only 10^{-5} a.u. or less from the smaller TZ to the largest QZ basis sets, which is probably comparable with the numerical noise of the computation. The change from simple restricted Hartree-Fock (RHF) values to correlated ones is of about 10^{-4} a.u. or less and is thus small with respect to our accuracy goal. Anyway, it may happen that the RHF error becomes much larger for geometries very far away from equilibrium where the single-determinant approximation of the wave function breaks down. All correlated methods agree between themselves at the level of 2×10^{-5} a.u. or better, so any one of these would be adequate. The fastest method and at the same time probably the most robust for geometries far away from equilibrium is CASSCF.

III. FITTING THE DMS

As discussed extensively by Schwenke and Partridge,[23] obtaining a good analytical fit to *ab initio* dipole data for water is a challenging problem, not least because the resulting surface must be able to reproduce dipole transition intensities which vary by many orders of magnitude. To represent the dipole surfaces $\boldsymbol{\mu}$ we used the analytic form introduced by Partridge and Schwenke,[11]

$$\boldsymbol{\mu}(r_1,r_2,\theta)=q(r_1,r_2,\theta)(\mathbf{x}_{H_1}-\mathbf{x}_O)+q(r_2,r_1,\theta)(\mathbf{x}_{H_2}-\mathbf{x}_O),$$
(1)

where the $\mathbf{x}$ vectors represent the atomic positions and (r_1,r_2,θ) are the internal coordinates represented by two bond lengths and the included angle, respectively. With this form the fitting problem reduces to parametrizing the scalar q functions, which is expressed as[11]

$$q(r_1,r_2,\theta)=\exp(-\beta r_e^2 x_1^2)\left\{\sum_{i=0}^{n_r}c_i x_1^i\right.$$
$$\left.+\exp(-\beta r_e^2 x_2^2)\sum_{i=0}\sum_{j=0}\sum_{k=0}c_{ijk}x_1^i x_2^j x_3^k\right\},$$
(2)

where r_e and θ_e are the equilibrium bond length and angle,

$x_i=(r_i-r_e)/r_e$ $(i=1,2)$, $x_3=\cos\theta-\cos\theta_e$, and $i+j+k\leq n_\theta$, $j+k>0$ and $i+j\leq n_r$.

A very large number of different fits were attempted. Many of them suffered from the problem, identified by Schwenke and Partridge,[23] of small unphysical oscillations in the fitted function. This problem, which occurs particularly in the angular coordinate, results in surfaces which artificially increase the intensity of the many weak transitions. We addressed this problem by comparing fitted surfaces with interpolations between our *ab initio* data. As mentioned above, extra *ab initio* calculations were performed at points where the discrepancy between these two was found to be particularly significant.

In our final fits we followed Schwenke and Partridge and augmented our calculations with extra points to ensure smoothness. These points were generated by plotting q for fixed r_1 and r_2 against $x=\cos(\theta)-\cos(\theta_e)$. The *ab initio* data were divided into sets with common values of r_1 and r_2. There were 140 sets with 7 or more x values. Within each of these sets a one-dimensional cubic spline was used to generate extra data on a grid of x values in steps of 0.02. Some 12 000 extra points were generated in this fashion.

Considerable experimentation was made with weighting functions. In the end a very simple formula was used. All *ab initio* data for geometries whose energy is 30 000 cm^{-1} or less above the potential minimum were given unit weight, all higher-lying points were excluded from the fit. Similarly, only interpolation-generated points for geometries up to 30 000 cm^{-1} were included in the fit; these points were weighted as $1/850$. Other more complicated energy-dependent weighting schemes, such as that proposed in Ref. 11 gave fits of worse or similar quality, so their use did not appear to be justified.

In the fits the exponent β was fixed at $0.420\,042\,8411a_0^{-2}$.[64] The resulting fit was performed with $n_r=8$ and $n_\theta=18$, giving 615 linear parameters. This fit reproduces the 878 *ab initio* dipole moments used in the fit with an average squared residual of 1.17×10^{-9} a.u. When the fitted DMS is used to reproduce the 369 points lying in the energy range 30 000–40 000 cm^{-1}, the average squared residual is 6.1×10^{-5} a.u. and it is 1.6×10^{-4} a.u. for the points whose energy is between 40 000 and 100 000 cm^{-1}.

The core correlation correction calculations were fitted to the functional form of Schwenke and Partridge.[23] Indices were not allowed to exceed a value of 6, resulting in an 84 parameter fit. Given the small relative magnitude of the correction a very high-accuracy fit was not required; the above fit gave mean square residual of 1.7×10^{-10} a.u. based on 355 points with 84 fitting parameters. The *ab initio* electronic relativistic correction calculations were fitted on the same basis as the core correction. The mean square residual of this fit is 2.4×10^{-10} a.u. based on 357 points with 84 fitting parameters. A FORTRAN routine containing our final DMS and the fitting parameters is given in EPAPS.[39]

IV. ROVIBRATIONAL WAVE FUNCTIONS

Rotation-vibration wave functions and dipole transition moments were computed using the nuclear motion program suite DVR3D.[65] The calculations were performed using the basis set parameters developed for the BT2 line-list calculations[25] which ensured tight convergence. Two distinct sets of wave functions were used in the tests presented below: those generated using the *ab initio* CVRQD PES (Refs. 13 and 15) and those generated using the spectroscopically determined FIS3 PES of Shirin *et al.*[12] Henceforth, the related wave functions are labeled CVRQD and FIS3, respectively. States with total rotational angular momentum J up to 9 were considered.

V. RESULTS AND DISCUSSION

All reported dipoles are in atomic units, with 1 a.u. $=2.541\,746$ D.

A. The DMS

Table V compares calculated DMSs for 14 key structures chosen to demonstrate the behavior of these surfaces. This table is testament both to the quality of our fit and to the fact that our individual dipole values lie close to those of SP2000. The table also shows that the core and relativistic corrections to the dipoles appear to be of similar magnitude but of opposite sign not only at equilibrium but also along the surface. This important phenomenon is explored further in Fig. 1. This figure shows that these two important corrections to the valence-only solution are indeed strongly anticorrelated and to a very significant extent cancel as a function of all three geometric parameters of water. As yet we have found no convincing explanation for this behavior.

B. Effect of PES on intensities

Comparisons with experiment are best made for dipole transition intensities rather than for the dipoles themselves. One issue that needs to be addressed here is the influence of rotation-vibration wave functions on intensities and hence the effect of PES used in the intensity calculations. To assess this we have analyzed the change in intensity predicted for the 340 $J=0–1$ transitions listed in HITRAN 2004 (Ref. 66) when using a dipole surface (either CVR or SP2000) and wave functions computed using the *ab initio* CVRQD surface or the spectroscopically determined FIS3 surface of Shirin *et al.*[12] For 334 of these lines, the effect of the wave function on the predicted transition intensity was only about 2%, with transitions computed using the CVRQD PES being systematically about 2% weaker. The remaining six lines, which are detailed in Table VI, show considerable sensitivity to the choice of the wave function. This behavior is a reflection of the effect of strong interaction between neighboring vibrational states ("resonances") which, in particular, can lead to strong enhancement of weak transitions. This coupling is particularly sensitive to the details of the PES but would appear to affect only about 2% of the transitions. Nevertheless, it reflects the difficulties one encounters in predicting intensities of exceedingly weak transitions which become increasingly the subject of experimental investigations due to the advances in relevant techniques. Below all calculations used the CVRQD PES unless otherwise stated.
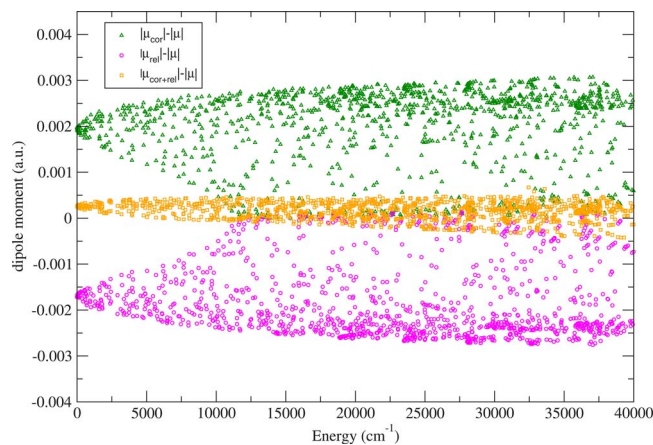
FIG. 1. (Color online) Comparison of the change in the dipole moment due to (a) the relativistic correction, (b) the core correction, and (c) the sum of these two effects plotted as function of the potential energy. The corresponding 1491 geometries are those for which the valence-only dipole moments were calculated. Value for the core and relativistic correction for these geometries were obtained from the respective correction surfaces.

C. Rovibrational transition intensities

The 2004 edition of the HITRAN database[66] provides a compilation of experimental results for $H_2^{16}O$. Comparison between transition intensities calculated using our final DMS surface CVR and the HITRAN data is given in Fig. 2.

A comparison between transitions computed with the SP2000 dipole surface and HITRAN looks very similar to that of Fig. 2. Figure 3 therefore gives instead a direct comparison between our CVR surface and SP2000 for the transitions between levels with $J \leq 9$ listed in HITRAN. It can be seen that the agreement between the two sets of theoretical data is much closer than their agreement with HITRAN. There is a very large dynamic range of the intensity of important water transitions. HITRAN, for example, lists transitions whose intensity differs by over 10 orders of magnitude at room temperature. It is therefore difficult to find a simple measure of reliability for a given DMS. After some experimentation we found that one suitable representation of this was to consider the distribution given by the ratio of the calculated intensity to the experimental one. Figure 4 presents the data of Fig. 2 in this fashion. It can be seen that the distribution is better fitted by a Lorentzian function than a Gaussian although the Lorentzian fit still remains not entirely satisfactory.

Representing the distribution by a Lorentzian function then gives an average error (the peak of the Lorentzian function) and an approximate error given by the full width at half maximum of the Lorentzian Γ. For the data given in Fig. 2 our intensities are 0.6% too strong with a Γ approximately corresponding to a width of $\pm 17\%$. These figures are almost identical to the results obtained if the calculation is repeated using the SP2000 DMS, which gives 0.6% and $\pm 16\%$, respectively. Indeed, there is a significantly higher correlation between results calculated with the two distinct DMSs than between the surfaces and HITRAN.

One interesting feature shown by the comparison of our results with HITRAN 2004, see Fig. 2, and the same comparison using SP2000, is the substructure at higher intensities suggesting some systematic disagreement. This substructure

TABLE V. Calculated dipole moments, in a.u., for a selection of 14 reference structures, as a function of the computational model.

No.	Sym	r_1 a_0	r_2 a_0	θ (deg)	RE[a] (cm^{-1})	μ_{AGZ} $\mu_\parallel$	$\mu_\perp$	μ_{fit} $\mu_\parallel$	$\mu_\perp$	$\Delta\mu_{rel}$ $\mu_\parallel$	$\mu_\perp$	$\Delta\mu_{cor}$ $\mu_\parallel$	$\mu_\perp$	μ_{tot} $\mu_\parallel$	$\mu_\perp$	μ_{SP2000} $\mu_\parallel$	$\mu_\perp$
1	C_{2v}	1.8096	1.8096	104.520	0	0.734 23	⋯	0.734 23	⋯	−0.001 71	⋯	0.001 97	⋯	0.734 49	⋯	0.733 38	⋯
2	C_{2v}	1.7008	1.7008	104.520	1 617	0.722 26	⋯	0.722 23	⋯	−0.001 51	⋯	0.001 78	⋯	0.722 50	⋯	0.721 50	⋯
3	C_{2v}	2.3622	2.3622	104.520	19 253	0.745 73	⋯	0.745 71	⋯	−0.002 57	⋯	0.002 65	⋯	0.745 80	⋯	0.744 28	⋯
4	C_{2v}	1.4173	1.4173	100.000	31 555	0.706 60	⋯	0.706 55	⋯	−0.001 09	⋯	0.001 35	⋯	0.706 81	⋯	0.705 99	⋯
5	C_{2v}	2.6456	2.6456	100.000	32 954	0.746 75	⋯	0.746 41	⋯	−0.002 72	⋯	0.002 84	⋯	0.746 53	⋯	0.744 71	⋯
6	C_{2v}	1.7952	1.7952	170.000	10 753	0.132 09	⋯	0.132 09	⋯	−0.000 34	⋯	0.000 31	⋯	0.132 07	⋯	0.132 12	⋯
7	C_{2v}	1.7952	1.7952	45.000	28 085	0.974 19	⋯	0.974 20	⋯	−0.002 16	⋯	0.002 48	⋯	0.974 52	⋯	0.972 60	⋯
8	C_s	1.7952	2.3622	179.900	24 624	0.001 40	−0.337 64	0.001 38	−0.337 61	−0.000 01	0.000 07	0.000 01	−0.000 12	0.001 38	−0.337 67	0.001 38	−0.337 18
9	C_s	1.6063	2.5511	104.520	18 251	0.748 09	−0.109 50	0.748 06	−0.109 49	−0.002 11	0.000 73	0.002 31	−0.000 79	0.748 26	−0.109 55	0.746 92	−0.108 58
10	C_s	1.7952	3.7795	104.520	34 086	0.556 37	0.199 03	0.556 76	0.228 45	−0.002 01	0.000 37	0.002 27	−0.000 40	0.557 02	0.228 41	0.419 56	0.459 73
11	C_{2v}	1.8120	1.8120	104.343	0.4	n/a	n/a	0.735 50	⋯	−0.001 71	⋯	0.001 97	⋯	0.735 76	⋯	0.734 63	⋯
12	C_s	1.4173	1.6063	120.000	18 715	0.605 47	−0.048 16	0.605 47	−0.048 14	−0.001 04	0.000 11	0.001 16	−0.000 17	0.605 59	−0.048 20	0.605 11	−0.048 06
13	C_s	1.5118	1.7008	100.00	8 973	0.735 37	−0.029 51	0.735 36	−0.029 51	−0.001 39	0.000 14	0.001 69	−0.000 18	0.735 66	−0.029 56	0.734 61	−0.029 40
14	C_s	2.7132	2.3622	95.000	14 408	0.810 38	−0.007 35	0.810 37	−0.007 34	−0.002 50	0.000 12	0.002 69	−0.000 13	0.810 56	−0.007 35	0.808 65	−0.007 12

[a]Relative energies (RE) are with respect to structure No. 1.

[b]$\mu_{tot} = \mu_{fit} + \Delta\mu_{rel} + \Delta\mu_{cor}$; $\mu_\parallel$ = component of μ parallel to the bisector of the HOH angle; and $\mu_\perp$ = component of μ perpendicular to the bisector of the HOH angle.

TABLE VI. Transition intensities involving states with $J=0$ and/or 1 which are highly sensitive to the details of the rotational-vibrational wave function. The wave functions were generated from the purely *ab initio* CVRQD potential (Refs. 13 and 15) or the spectroscopically determined semitheoretical FIS3 potential of Shirin *et al.* (Ref. 12). All transitions are from the (0 0 0) vibrational ground state. Powers of ten are given in parentheses.

| | | | | | Line intensities (cm molecule^{-1}) | | | | |
| | | | | | | CVR | | SP2000 | |
$v_1' v_2' v_3'$	$J' K_a' K_c'$	$J'' K_a'' K_c''$	Wavenumbers (cm^{-1}) HITRAN	HITRAN	CVRQD	FIS3	CVRQD	FIS3
0 7 1	000	101	13 811.5791	2.02(−25)	1.86(−26)	1.59(−25)	3.51(−26)	2.03(−25)
4 0 0	111	000	13 861.6677	1.31(−25)	5.75(−27)	9.92(−26)	1.10(−26)	1.26(−25)
0 5 3	111	110	18 374.5704	6.45(−27)	1.47(−26)	9.11(−27)	6.75(−27)	3.29(−27)
4 0 2	110	101	20 546.5874	1.06(−26)	9.58(−30)	5.09(−30)	1.06(−26)	1.09(−26)
6 0 1	111	110	22 517.8957	6.79(−26)	3.59(−29)	6.67(−26)	4.37(−28)	7.94(−26)
6 0 1	110	111	22 527.8971	3.19(−26)	1.06(−30)	2.90(−26)	5.92(−29)	3.24(−26)

occurs for the recent mid-infrared measurements of Toth.[67] No such systematic differences are found for data reported from any other source lying at either lower or higher frequency than this. The source of this systematic discrepancy remains to be determined.

A particularly stringent test of the DMS is given by a comparison with the work of Kassi *et al.*[68] on the absorption of water vapor near 13 320 cm^{-1}, since this spectrum probes particularly weak transitions and it is such weak transitions which are particularly sensitive to the details of the fit, see the extensive discussion of this by Schwenke and Partridge.[23]

Figure 5 compares the predicted CVR intensities for this spectrum with those of SP2000. We recomputed the SP2000 results but obtained results very similar to those quoted by Kassi *et al.*[68] For the stronger portion of this spectrum, intensities above 10^{-27} cm molecule^{-1}, the CVR DMS clearly gives better agreement than SP2000: on average 3% stronger with $\Gamma=27\%$ against 14% stronger and $\Gamma=39\%$ for SP2000. Below 10^{-28} cm molecule^{-1} both DMSs do less well, although ours again performs better, 16% average error with $\Gamma=52\%$ against 31% average error and $\Gamma=68\%$. A direct comparison between the CVR and SP2000 DMSs for these lines suggests that our intensities are about 10% less; even with this we are still overestimating the strength of weaker lines by about 15%.
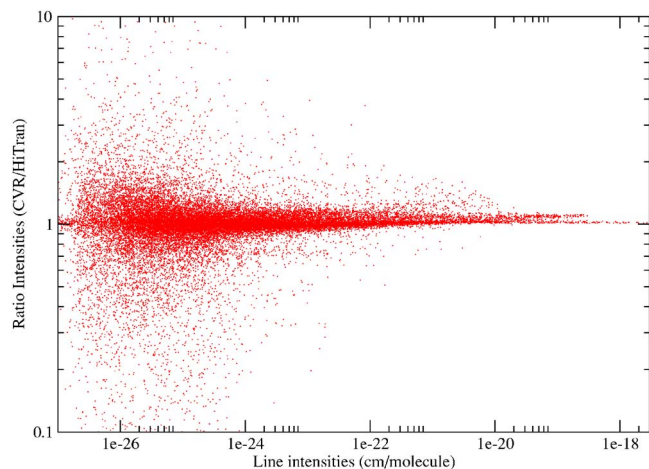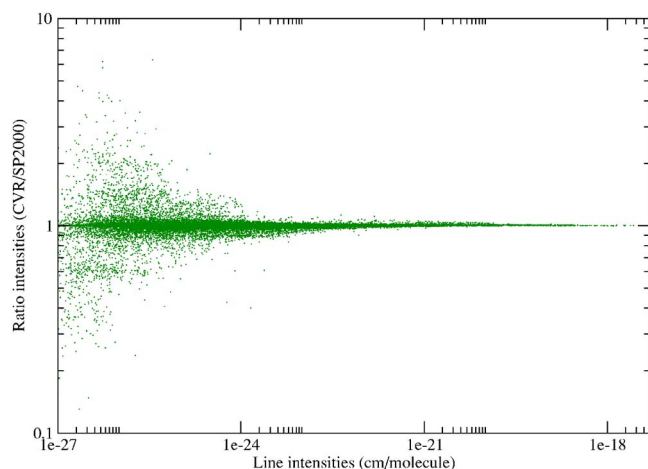

FIG. 3. (Color online) Ratio of dipole line intensities predicted by the CVR dipole surface and that of Schwenke and Partridge (Ref. 23) for $H_2^{16}O$ lines reported in the 2004 version of the HITRAN database (Ref. 66).

FIG. 2. (Color online) Ratio of dipole line intensities for $H_2^{16}O$ predicted by the CVR dipole surface to those reported in the 2004 version of the HITRAN database (Ref. 66).
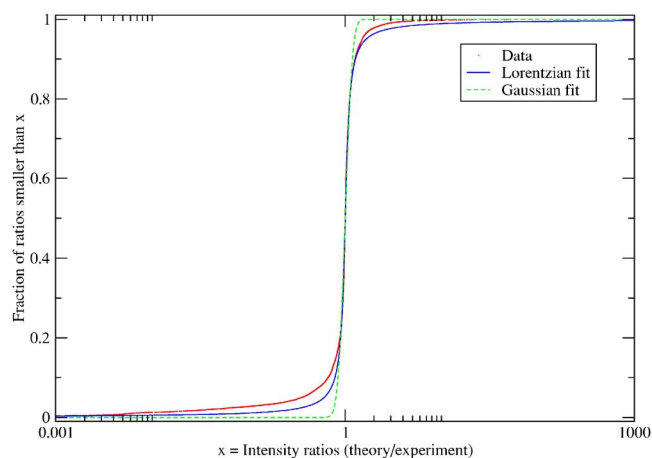

FIG. 4. (Color online) Distribution of ratio between the CVR dipole line intensities and those reported in the 2004 version of the HITRAN database (Ref. 66).
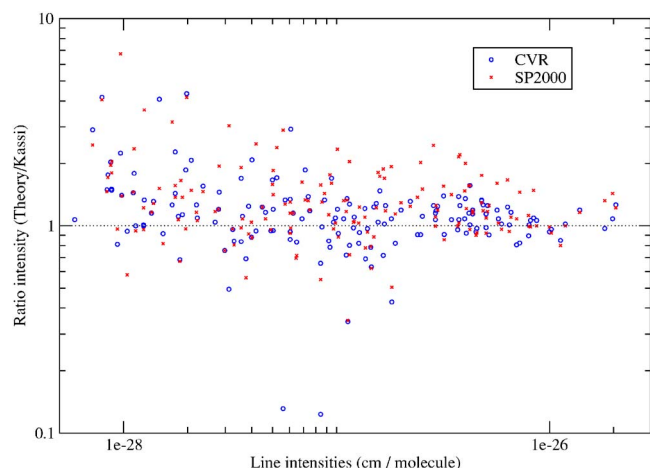
FIG. 5. (Color online) Comparison of intensity predictions of our DMS surface with that of Schwenke and Partridge (Ref. 23) for the spectrum of Kassi *et al.* (Ref. 68).

It should be noted that this comparison is not entirely straightforward since SP's intensities were used to assign the Kassi *et al.* spectrum which can lead to some systematic bias. Indeed, there are four lines, see Table VII, for which we obtain very significantly weaker intensities suggesting that the line may have been wrongly assigned because their predicted intensity was overestimated.

D. Equilibrium dipole moment of water

As an independent test of the quality of our DMS we computed a highly accurate value of the dipole moment of water and confronted it with that of the CVR DMS and with the best available experimental data. The quantity that is directly related to the experimental dipole is given by the average of the DMS over the ground-state rovibrational nuclear-motion wave function. In the assumption that the shape of our DMS is essentially correct for geometries close to equilibrium and that the main effect with respect to a second DMS is a global shift, we can estimate the value of the vibrational averaged dipole for a new surface by calculating a value for a single reference structure (near equilibrium) and then adding the difference between vibrationally averaged value computed with the existing DMS and the value of the existing DMS for the reference geometry. It should be noted that the value of this vibrational correction is sensitive to the choice of reference structure and therefore has little meaning on its own. As reference structure for all

TABLE VIII. Dipoles at the reference structure $r=0.95782$ Å and $\theta=104.485°$.

	Value (a.u.)	Uncertainty (a.u.)
Nonrelativistic, all electron	0.7310	0.0005
Relativistic correction	−0.0017	0.0001
Vibrational averaging	0.0001	0.0001
Final value for the ground-state dipole	0.7294	0.0006
Experimental value	0.7296	0.0002

our equilibrium dipole moment calculations of this section we used the best estimate of the Born-Oppenheimer equilibrium geometry of $H_2{}^{16}O$, as given in Ref. 69, that is $r_e=0.95782$ Å and $\alpha_e=104.485°$.

As is clear from Tables I, III, and IV, the equilibrium dipole of water can be computed with reasonable accuracy, i.e., within 10^{-3} a.u., at relatively low levels of theory. This is due to the fact that the dipole moment of water is relatively insensitive to basis set size. Once diffuse (low-exponent) Gaussian functions are included in the basis, the computed dipole changes little with the different cardinal numbers of the basis. The effect of introduction of tight (core) functions into the basis is especially small. It is also clear that basis set and electron correlation effects are rather well separated, thus the usual additivity assumption[33] about these increments seems to hold well.

An accurate nonrelativistic all-electron Born-Oppenheimer value, 0.7310 ± 0.0005 a.u., has been obtained for water in this study (see Table VIII). This value was determined by extrapolating the aug-cc-pCV5Z and aug-cc-pCV6Z CCSD(T) dipoles to the complete basis set (CBS) limit using a two-point polynomial formula with X^{-3} and adding to this extrapolated value of the aug-cc-pCVDZ CCSDTQ-CCSD(T) difference. Clearly, the dipole moment of water seems to be converged at the CCSDTQ level. Furthermore, basis set enlargement beyond the aug-cc-pCV6Z level seems to change the dipole only by a small amount, 0.0005 D at the CCSD(T) level. Using the same extrapolation scheme with the IC-MRCI+Q values relative to the CAS3 of Table I yields a value of 0.7307 a.u., hence consistent with the coupled-cluster value within the assumed error bar. This value should be compared with the all-electron equilibrium dipole of the CVR DMS, 0.73645 a.u. The two

TABLE VII. Transitions from Kassi *et al.* (Ref. 68) for which we obtain significantly different intensities. All transitions are from the (0 0 0) vibrational ground state. Powers of ten are given in parentheses.

$v_1' v_2' v_3'$	$J' K_a' K_c'$	$J'' K_a'' K_c''$	Wavenumbers (cm^{-1})		Line intensities (cm/molecule)		
			Obs[a]	Calc.[b]	Obs[a]	This work	SP2000
0 4 2	606	615	13 351.5063	13 351.6631	1.86(−28)	1.82(−29)	3.06(−28)
0 4 2	221	330	13 361.8032	13 362.0395	8.43(−28)	1.04(−28)	1.32(−27)
0 4 2	220	331	13 362.9934	13 363.2152	6.45(−28)	3.56(−29)	4.50(−28)
0 4 2	505	514	13 376.2655	13 376.4261	5.61(−28)	7.34(−29)	1.62(−27)

[a]Reference 68.
[b]Reference 12.

TABLE IX. Vibrationally averaged dipole moments, in a.u., as function of (a) potential energy surface used to provide the $H_2^{16}O$ vibrational wave function and (b) the dipole moment surface used.

PES	μ_{6Z}	$\mu_{6Z} + \Delta\mu_{rel} + \Delta\mu_{cor}$	μ_{SP3000}[a]
Shirin2003[b]	0.734 55	0.734 80	0.733 66
CVRQD[c,d]	0.734 53	0.734 78	0.733 64

[a]Reference 23.
[b]Reference 12.
[c]Reference 13.
[d]Reference 15.

values are in reasonably good agreement. The relativistic contribution to these values, -0.0017 ± 0.0001 a.u., was computed from the CVR DMS.

Table IX compares dipoles computed with different surfaces and averaged using vibrational wave functions generated using the CVRQD *ab initio* PES (Refs. 13 and 15) and the FIS3 semiempirical PES of Shirin *et al.*[12] It can be seen that the change due to which vibrational wave function is used is about 2×10^{-5} a.u. and thus is very small.

There have been a number of reported experimental values for the dipole moment of the water molecule. The 1973 Stark measurement of Clough *et al.*[70] gave 1.8546(6) D (=0.7297 a.u.). This study probably remains the most accurate performed to date. It is consistent with the more recent values of 1.854 D (=0.7294 a.u.) of Lovas[71] and 1.855 D (=0.7303 a.u.) of Gregory *et al.*[72] Table VIII gives 0.7296 ± 0.0002 a.u. for the experimental dipole moment of water corresponding to the weighted average of these three measurements. Our best theoretical estimate of 0.7294 ± 0.0006 a.u. agrees with the experimental value within the respective error bars.

VI. SUMMARY

A first-principles dipole moment surface (DMS) has been obtained for water, based principally on aug-cc-pV6Z IC-MRCI valence-only dipole moment computations, augmented with core and relativistic corrections. The core corrections utilized the size-extensive CCSD(T) method. After extensive testing, the relativistic corrections were based on spin-free Dirac-Coulomb calculations. The equilibrium dipole moment of water given by this DMS is 0.7365 a.u., slightly larger than our own best estimate of the equilibrium dipole of water, 0.7310(5) a.u., based on an extensive set of higher-order coupled-cluster computations performed at the best estimate of the Born-Oppenheimer equilibrium structure of $H_2^{16}O$. Adding the small vibrational correction to the equilibrium dipole gives a ground-state dipole for $H_2^{16}O$ of 0.7294(6) a.u. in nice agreement with the best experimental estimate of the vibrationally averaged dipole moment of water, 0.7297(3) a.u..[70]

In test calculations over large data sets our CVR DMS performs comparably to the best previous DMS of water, SP2000.[23] This is due to the fact that the two distinguishing features of the new DMS, (a) inclusion of core and relativistic effects and (b) use of a considerably larger basis for the valence-only dipole computations, both have an overall almost negligible effect. Basis set dependence of the dipole is

minuscule between the truncated cc-pV5Z and aug-cc-pV6Z, and core and relativistic effects cancel each other over almost the whole configuration space considered. More studies on a large set of smaller molecular systems is needed to explain this interesting cancellation of core and relativistic effect.

The CVR DMS does perform better than SP2000 at predicting the intensities of very weak overtone transitions. This is probably due to the fact that our fit function is somewhat smoother than that used in the earlier study. Strategies to smoothly interpolate between the grid points to produce a DMS completely free of small oscillations are still required.

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[39] See EPAPS Document No. E-JCPSA6-127-307747 for (1) a FORTRAN program of the CVR DMS surface, (2) the computer au-cc-pV6Z MRCI dipoles, and (3) the relativistic and core correction dipoles. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

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