

The barrier to linearity of water

György Tarczay and Attila G. Császár^{a)}

Department of Theoretical Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

Wim Klopper^{b)}

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Viktor Szalay

Crystal Physics Department, Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1523 Budapest, Hungary

Wesley D. Allen and Henry F. Schaefer III

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

(Received 8 December 1998; accepted 4 February 1999)

High-quality *ab initio* quantum chemical methods, including higher-order coupled cluster (CC) and many-body perturbation (MP) theory, explicitly correlated (linear R12) techniques, and full configuration interaction (FCI) benchmarks, with basis sets ranging from [O/H] [3s2p1d/2s1p] to [8s7p6d5f4g3h2i/7s6p5d4f3g2h] have been employed to obtain the best possible value for the barrier to linearity of water. Attention is given to the degree of accord among extrapolations of conventional MP2, CCSD, and CCSD(T) energies to the complete basis set (CBS) limit and corresponding linear R12 schemes for these correlation methods. Small corrections due to one- and two-particle relativistic terms, core correlation effects, and the diagonal Born–Oppenheimer correction (DBOC) have been incorporated. The final electronic (vibrationless) extrapolated barrier height of this study is $11\,127 \pm 35 \text{ cm}^{-1}$. Anharmonic force fields have been determined at the aug-cc-pCVTZ CCSD(T) level at equilibrium and at a linear reference geometry. These and previous sextic force fields are in general accord with the expansion terms of recent global potential energy hypersurfaces but also highlight some of their weaknesses. © 1999 American Institute of Physics. [S0021-9606(99)30917-X]

I. INTRODUCTION

Recently, the precise determination of the potential energy (hyper)surface (PES) of the ground electronic state of water has received renewed interest,^{1–7} due to drastically increased spectroscopic capabilities for detecting higher-lying bending states,^{8,9} publicity over the extremely dense manifolds of rovibrational states recorded and recently analyzed in the sunspot spectrum of water,^{4,10} and the special role the water molecule plays in the physics and chemistry of combustion systems, the interstellar medium, and the atmospheres of planets and cool stars.¹¹ The ground-state PES of water has traditionally been a testing ground for the myriad theoretical approaches for computing (ro)vibrational eigenstates, resulting in a large number of publications on local and global surfaces.^{1–3,6,12–25} These studies have shown that even small physical effects usually neglected during construction of PESs, such as relativistic phenomena³ and non-Born–Oppenheimer terms,¹ may produce changes on the order of a few cm^{-1} for rovibrational eigenstates.

Among the numerous studies on highly excited vibrational states, there are several reports on the barrier to linearity of water.^{2,6,15,17,26,27} In one of the early empirical vibrational studies of the energy levels of water, Carter and

Handy¹⁵ obtained $11\,493 \text{ cm}^{-1}$ for the barrier height. Another empirical estimate, $11\,597 \text{ cm}^{-1}$ (Ref. 17) was obtained via direct least-squares fits of 19 parameters of the variational Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian to 550 experimental energy separations, which involved $J \leq 2$ levels in 103 vibrational manifolds of six isotopomers, with energies up to $19\,000 \text{ cm}^{-1}$ above the (0,0,0) state. The barrier of $11\,597 \text{ cm}^{-1}$ was obtained from the MORBID bending potential with bond lengths fixed at their equilibrium values; therefore, it is hard to compare it with electronic (vibrationless) barriers. Two recent, exceedingly high-quality PESs of water resulted in vibrationless barrier heights of $10\,966$ (Ref. 2) and $11\,128$ (Ref. 6) cm^{-1} . Polyansky, Jensen, and Tennyson² deduced, through a variational scheme using the exact kinetic energy operator, a highly-accurate empirical PES of water, usually denoted as PJT2, which represents 3200 experimentally observed low- and high-lying rovibrational states of water with a standard deviation of only 0.25 cm^{-1} . Initial values of the parameters of the PJT2 potential were taken from *ab initio* calculations of medium quality.¹⁷ Some highlights of the high-quality *ab initio* calculations on which the semiempirical (actually semitheoretical) PES of Partridge and Schwenke (PS) (Ref. 6) is based are as follows: (a) use of the correlation-consistent cc-pV5Z basis set augmented with diffuse *s*, *p*, and *d* functions on O and *s* and *p* sets on H, followed by estimation of the complete basis set (CBS) limit;

^{a)} Author to whom correspondence should be addressed.

^{b)} Present address: Theoretical Chemistry Group, Debye Institute, Utrecht University, Padualaan 14, NL-3584 CH Utrecht, The Netherlands.

(b) optimization of the orbitals using a complete active space self-consistent-field (CASSCF) approach, giving a balanced description for all geometries; (c) inclusion of electron correlation through the internally contracted multireference configuration interaction (ICMRCI) approach, augmented by a multireference Davidson correction; (d) evaluation of core correlation effects through a set of averaged coupled pair functional (ACPF) calculations. There is a dearth of high-energy rovibrational data for the adjustment of the PJT2 and PS surfaces, and thus the current surfaces contain some “extrapolation” into regions of no or limited data, such as the region around linearity. The sizable difference between reported literature values for the barrier to linearity, and the fact that quantity has a significant effect³ on the calculation of even low-lying bending states, calls for a careful, state-of-the-art *ab initio* quantum chemical investigation of the barrier height of water. It is expected^{26–28} that extrapolated relative energy predictions based on electronic structure calculations can have an accuracy perhaps an order of magnitude better than the spread in the aforementioned estimates for the barrier. Therefore, one goal of this study is to approach this *ab initio* limit as closely as technically possible.

In order to arrive at the *ab initio* quantum chemical limit for energy differences such as the barrier to linearity of water, a systematic layout must be made of the dual basis set and electron correlation convergence, preferably including physically motivated extrapolations to the complete basis set (CBS) and full configuration interaction (FCI) asymptotes. The best possible *ab initio* predictions then require auxiliary corrections for effects tacitly neglected in most theoretical work, including core correlation, special relativity, and the diagonal Born–Oppenheimer correction (DBOC). The capability of current *ab initio* methods in pinpointing prototypical energy differences on the potential energy surfaces of ammonia, water, ethane, isocyanic acid, formic acid, and silicon dicarbide has been the focus of recent investigations.^{26–28} For the problem of the water barrier, the present study pushes *ab initio* methodologies to new heights. For example, the CBS asymptote is investigated via a comparative study of conventional extrapolations and explicitly correlated calculations, while relativistic corrections, which are quite important for the water barrier, are investigated through two-body terms in order to assess the issues involved in their computation via perturbation theory.

Naturally, the aforementioned *ab initio* calculations result directly in estimates of the electronic (vibrationless) barrier height. These values can directly be compared to the best empirical (e.g., Ref. 2) and semitheoretical (e.g., Ref. 6) PESs, since they are also complete-dimensional, vibrationless surfaces. While the barrier is a crucial parameter characterizing global PESs of water, assessment of the available hypersurfaces can be enhanced by other means of electronic structure theory. Most importantly, anharmonic force field representations of these hypersurfaces, when compared to high-quality *ab initio* force fields,²⁹ provide critical assessment of the accuracy of the analytic PESs (Refs. 2 and 6) in the immediate vicinity of the reference (bent and linear) structures. This comparison forms another important part of this paper.

II. CLASSICAL INVERSION BARRIER

The conventional electronic structure computations reported in this paper were performed with the ACES II,³⁰ PSI,³¹ and GAUSSIAN 94 (Ref. 32) program systems. The explicitly correlated (linear R12) calculations utilized the program packages SORE (Ref. 33) and DIRCCR12.³⁴ From results obtained with the two standard approximations (R12/A and R12/B) of linear R12 methods,³⁵ only the R12/B energy values are reported for the valence-only calculations.

Reference electronic wave functions were determined by the single-configuration restricted Hartree–Fock (RHF) method.³⁶ Dynamical electron correlation was accounted for by Møller–Plesset (MP) perturbation theory from second through fifth order (MP2–MP5),³⁷ by the coupled cluster (CC) method³⁸ including all single and double (CCSD) (Refs. 38 and 39) and triple excitations (CCSDT),⁴⁰ or by configuration interaction computations (CISD, CISDT, CISDTQ, CISDTQP, and FCI).⁴¹ The CCSD(T) method,⁴² which estimates the effect of connected triple excitations through a perturbative term, was employed extensively. The Brueckner doubles (BD) method^{43,44} with perturbational estimates for both connected triple and quadruple excitations [BD(TQ)] [Ref. 37(c)] was also employed. Extrapolation of the MP n series,⁴⁵ resulting in MP ∞ , was performed via shifted [2,1] Padé approximants when fifth-order energies were available. In valence-only correlated-level calculations the 1s core orbital of oxygen was kept doubly occupied. No virtual molecular orbitals were frozen in any of the correlation treatments.

The basis sets chosen for the calculations include the correlation-consistent (aug)-cc-p(C)VXZ families of basis sets developed by Dunning and co-workers.⁴⁶ The largest of the basis sets employed here, aug-cc-pV6Z, includes basis functions with angular momenta up to i on oxygen and h on hydrogen. The corresponding number of basis functions is 443, as compared to 24 functions in the smallest (cc-pVDZ) set. Due to the factorial dependence of the n -particle space on the number of orbitals, the higher-order and full configuration interaction computations, which were performed by DETCI (Ref. 47) running within PSI,³¹ were executed with the cc-pVDZ and cc-pV(T/D)Z basis sets, the latter consisting of cc-pVTZ on O and cc-pVDZ on H. The number of determinants in the cc-pVDZ FCI and cc-pV(T/D)Z CISDTQP computations for bent, C_{2v} (linear, $D_{\infty h}$) water were 19 604 169 (9 802 897) and 55 711 395 (27 854 673), respectively, representing the largest CI calculations of the present study. R12 calculations also employed specially designed [O/H] = [13s8p6d5f/7s5p4d] and [15s9p7d5f/9s7p5d] Gaussian basis sets denoted here as K1 [Ref. 48(a)] and K2,^{48(b)} respectively. The K1 and K2 basis sets are almost saturated at the level of *spdf* functions but contain no functions of higher angular momentum. They were specifically designed for linear R12 calculations, therefore, using traditional methods their convergence behavior might be drastically different from that of the correlation-consistent basis sets.

Reference geometries for the energy calculations have been obtained at the all-electron aug-cc-pVTZ CCSD(T) level. The geometric parameters employed for the single-point energy and energy correction calculations are as fol-

TABLE I. The effect of basis set size and electron correlation on the inversion barrier of water.^a

| Series I | $\Delta E_c(\text{RHF})$ | $\delta[\text{MP2}]$ | $\delta[\text{CCSD}]$ | $\delta[\text{CCSD(T)}]$ | $\delta[\text{CCSDT}]$ | $\delta[\text{BD(TQ)}]$ | $\Delta E_c(\text{CC})$ |
|----------------------|--------------------------|-----------------------|------------------------|--------------------------|--------------------------|---------------------------|-------------------------|
| cc-pVDZ(24) | 12 206 | +352 | +173 | +94 | +6 | +4 | 12 835 |
| cc-pV(TZ/DZ)(40) | 11 639 | -205 | +265 | +28 | +2 | +7 | 11 736 |
| cc-pVTZ(58) | 11 519 | +102 | +189 | +54 | +2 | +4 | 11 870 |
| aug-cc-pVDZ+ICP(59) | 11 607 | -153 | +248 | +1 | [+2] | [+4] | [11 709] |
| aug-cc-pVTZ(92) | 11 280 | -144 | +266 | -11 | +3 | +19 | 11 413 |
| cc-pVQZ(115) | 11 350 | -128 | +212 | +17 | +3 | [+19] | [11 473] |
| aug-cc-pVTZ+ICP(138) | 11 269 | -218 | +270 | -14 | [+3] | [+19] | [11 329] |
| aug-cc-pVQZ(172) | 11 254 | -267 | +257 | -15 | [+3] | [+19] | [11 244] |
| K1 R12/B(186) | 11 236 | -354 | +316 | -8 | [+3] | [+19] | [11 212] |
| cc-pV5Z(201) | 11 248 | -257 | +250 | -5 | [+3] | [+19] | [11 258] |
| K2 R12/B(222) | 11 241 | -336 | +322 | -5 | [+3] | [+19] | [11 243] |
| aug-cc-pVQZ+ICP(264) | 11 256 | -301 | +270 | -17 | [+3] | [+19] | [11 230] |
| K1+ICP R12/B(270) | 11 239 | -340 | +299 | -17 | [+3] | [+19] | [11 203] |
| aug-cc-pV5Z(287) | 11 249 | -301 | +266 | -16 | [+3] | [+19] | [11 215] |
| cc-pV6Z(322) | 11 244 | -306 | +265 | -12 | [+3] | [+19] | [11 213] |
| K2+ICP R12/B(332) | 11 243 | -344 | +305 | -17 | [+3] | [+19] | [11 209] |
| aug-cc-pV6Z(443) | 11 248 | -330 | | | [+3] | [+19] | |
| aug-cc-pV5Z+ICP | 11 249 | -324 | +276 | -17 | [+3] | [+19] | [11 206] |
| CBS ^b | 11 246 | -348 | +283 | -17 | [+3] | [+19] | [11 186] |
| CBS ^c | 11 247 | -371 | +283 | -22 | [+3] | [+19] | [11 159] |
| Series II | $\Delta E_c(\text{RHF})$ | $\delta[\text{MP2}]$ | $\delta[\text{MP3}]$ | $\delta[\text{MP4}]$ | $\delta[\text{MP5}]$ | $\delta[\text{MP}\infty]$ | $\Delta E_c(\text{MP})$ |
| cc-pVDZ(24) | 12 206 | +352 | +117 | +155 | -2 | +5 | 12 833 |
| cc-pV(T/D)Z(40) | 11 639 | -205 | +148 | +153 | -23 | +14 | 11 726 |
| cc-pVTZ(58) | 11 519 | +102 | +87 | +180 | -43 | +18 | 11 863 |
| aug-cc-pVTZ(92) | 11 280 | -144 | +161 | +79 | +24 | -1 | 11 399 |
| aug-cc-pVQZ(172) | 11 254 | -267 | +145 | +86 | [+24] | [-1] | [11 241] |
| aug-cc-pV5Z(287) | 11 249 | -301 | +149 | +93 | [+24] | [-1] | [11 213] |
| aug-cc-pV6Z(443) | 11 248 | -330 | [+149] | [+93] | [+24] | [-1] | [11 183] |
| CBS ^d | 11 247 | -370 | +154 | +103 | [+24] | [-1] | [11 157] |
| Series III | $\Delta E_c(\text{RHF})$ | $\delta[\text{CISD}]$ | $\delta[\text{CISDT}]$ | $\delta[\text{CISDTQ}]$ | $\delta[\text{CISDTQP}]$ | $\delta[\text{FullCI}]$ | $\Delta E_c(\text{CI})$ |
| cc-pVDZ(24) | 12 206 | +459 | +89 | +76 | +5 | +1 | 12 836 |
| cc-pV(T/D)Z(40) | 11 639 | +8 | +19 | +69 | +1 | [+1] | [11 737] |

^aFor each basis set the total number of contracted Gaussian functions is given in parentheses. ICP refers to intramolecular counterpoise-corrected calculations (see text). For correlated-level calculations the symbol δ denotes the increment in the relative energy (ΔE_c) with respect to the preceding level of theory as given by the hierarchy RHF \rightarrow MP2 \rightarrow CCSD \rightarrow CCSD(T) \rightarrow CCSDT \rightarrow BD(TQ), RHF \rightarrow MP2 \rightarrow MP3 \rightarrow MP4 \rightarrow MP5 \rightarrow MP ∞ , and RHF \rightarrow CISD \rightarrow CISDT \rightarrow CISDTQ \rightarrow CISDTQP \rightarrow CISDTQPH \rightarrow FullCI, for Series I, Series II, and Series III, respectively. Brackets signify assumed increments from smaller basis set results. In Series I, the $\delta[\text{MP2}]$, $\delta[\text{CCSD}]$, and $\delta[\text{CCSD(T)}]$ increments refer to R12/B calculations for basis sets K1, K2, K1+ICP, and K2+ICP. All values are given in cm^{-1} .

^bThe complete basis set (CBS) RHF barrier is obtained by extrapolation of aug-cc-pV(T,Q,5)Z+ICP energies using Eq. (1). The CBS correlation increments are obtained by extrapolation of aug-cc-pV{Q,5}Z+ICP results using Eq. (2).

^cThe complete basis set (CBS) RHF barrier is obtained by extrapolation of aug-cc-pV(Q,5,6)Z energies using Eq. (1). The CBS correlation increments are obtained by extrapolation of cc-pV{5,6}Z results using Eq. (2).

^dThe complete basis set (CBS) RHF barrier is obtained by extrapolation of aug-cc-pV(Q,5,6)Z energies using Eq. (1). The CBS MP2 and (MP3, MP4) correlation increments are obtained by extrapolation of aug-cc-pV{5,6}Z and aug-cc-pV{Q,5}Z results, respectively, using Eq. (2).

lows: $r(\text{O}-\text{H})=0.958\,85(0.934\,11)\text{ \AA}$ and $\angle(\text{H}-\text{O}-\text{H})=104.343(180.0)^\circ$ in the $C_{2v}(D_{\infty h})$ cases.²⁶ The frozen-core K1 CCSD(T)-R12/B optimizations yield $r(\text{O}-\text{H})=0.9581(0.9340)\text{ \AA}$ and $\angle(\text{H}-\text{O}-\text{H})=104.45(180.0)^\circ$ in the $C_{2v}(D_{\infty h})$ cases. This comparison clearly suggests that geometry effects due to the inclusion of linear R12 terms are small. The differences between the barrier heights at the reference structures and at the respective optimized structures are less than 2 cm^{-1} , e.g., it is a mere 0.3 cm^{-1} at the K1 CCSD(T)-R12/B and K2 MP2-R12/A levels. As Tables IV and V (vide infra) indicate, relativistic corrections also have no significant effect on the bent and linear geometric parameters; for example, at the linear structure the relativistic bond length correction is only $1 \times 10^{-4}\text{ \AA}$. The DBOC corrections are expected to result in an even smaller geometric effect.

These considerations justify the use of the above fixed reference structures during valence focal-point energy calculations. The C_{2v} geometric parameters also compare favorably with available empirical equilibrium values, such as $r(\text{O}-\text{H})=0.958\,43\text{ \AA}$ and $\angle(\text{H}-\text{O}-\text{H})=104.4398^\circ$.⁴⁹

The entire valence *ab initio* analysis of the barrier to linearity is laid out in Table I. Auxiliary corrections to the barrier height due to core correlation and relativistic effects are collected in Tables II and III, respectively.

A. Valence *ab initio* limits

In their recent study on conformational energy prototypes, Császár, Allen, and Schaefer²⁶ employed the concept of focal-point analysis²⁸ to arrive at the one- and *n*-particle *ab initio* limits of relative energy predictions for the molecu-

TABLE II. Contribution of core correlation to the inversion barrier of water.^a

| Basis | MP2 | MP2-R12/A | CCSD | CCSD(T) | CCSDT |
|---------------|------|-----------|------|---------|-------|
| cc-pCVDZ(28) | -30 | | -25 | -25 | -25 |
| cc-pCVTZ(71) | -96 | | -89 | -87 | -85 |
| cc-pCVQZ(144) | -106 | | -97 | -95 | |
| K1(186) | -106 | -110 | | | |
| K2(222) | -106 | -109 | | | |

^aSee footnote a of Table I for details. Additional core correlation results are available from Ref. 26.

lar systems ammonia, water, ethane, isocyanic acid, formic acid, and silicon dicarbide. Details of this approach are as follows: (a) use of hierarchical families of basis sets which systematically approach completeness; (b) application of relatively low correlated levels of electronic structure theory with basis sets pushed to technical limits; (c) higher-order valence-only correlation treatments with the largest feasible basis sets; (d) layout of a two-dimensional extrapolation grid based on an assumed separability and additivity of correlation increments to the energy difference of concern; and (e) inclusion of auxiliary corrections physically important for the problem.

The results presented in Ref. 26 highlighted molecular prototypes which exhibit four different types of focal-point behavior. The determinations of the torsional barrier of ethane and the *E/Z* rotamer separation of formic acid were the easiest problems for molecular quantum chemistry, as both quantities showed limited basis set variation past the cc-pVQZ level and small correlation increments past MP4 (less than 0.1 kcal mol⁻¹ on both accounts). The determination of the barrier to linearity of the polytopic molecule SiC₂ (Ref. 50) was on the other end of the spectrum, as large variations, on the order of 1 kcal mol⁻¹, were observed for both extrapolations. The problem of converging the inversion barrier of water proved somewhat less demanding, as correlation increments past the MP4 level (i.e., after inclusion of triple excitations) were small. Nevertheless, basis set variation past the cc-pVQZ set was found to be very troublesome. Thus, the slow convergence toward the CBS limit of traditional quantum chemical methods seems to be the only real obstacle for the accurate prediction of the barrier to linearity of water. The linear R12 (Refs. 51–54) and Gaussian geminal^{55,56} methods have been designed to circumvent the slow basis set convergence problem of traditional electron

correlation techniques, and thus offer hope in arriving at a highly accurate barrier height for water. Linear R12 methods have been utilized in this study to assess and extend the previous focal-point analysis (FPA) results.²⁶

Data for the extended valence focal-point analysis of the barrier to linearity of water are collected in Table I. Three *n*-particle series have been investigated; coupled-cluster theory (CC; Series I), Møller–Plesset perturbation theory (MP; Series II), and configuration interaction theory (CI; Series III). The most balanced treatments are afforded by using CC wave functions. The data obtained by traditional techniques of electron correlation theory reveal the following:

- (1) Systematic extension of the basis set lowers the barrier to linearity of water at each level of theory. Nevertheless, upon enlargement of the one-particle basis set, the most dramatic changes appear at the RHF and especially the MP2 levels.
- (2) While smaller basis set results indicate that electron correlation increases the height of the barrier, results obtained with basis sets larger than cc-pVQZ show a small, overall correlation effect serving to lower the barrier.
- (3) Basis set extrapolations (see below) reveal that in the basis set limit the {RHF, CCSD} levels yield {100.65, 100.08}% of the extrapolated relative energy (ΔE_e) of 11 172 cm⁻¹ (vide infra). Therefore, in the particular case of the inversion barrier of water, RHF theory works extremely well due to fortuitous error cancellation. This behavior is certainly not typical when a larger body of molecular systems is studied.²⁶
- (4) For this system containing spatially active electron pairs, the aug-cc-pVXZ basis sets prove commensurate in accuracy with the larger cc-pV(X+1)Z sets, revealing the importance of diffuse functions in reaching convergence. Although concern has recently arisen regarding possible divergence of aug-cc-pVXZ absolute MP_{*n*} correlation energy series,⁵⁷ very smooth convergence patterns are observed in our focal-point analysis, where characteristics of relative energy changes are of concern.
- (5) The traditional δ [MP2] increment does not converge within even a modest 0.1 kcal mol⁻¹ target until the basis set is extended drastically, well beyond the cc-pV6Z level.
- (6) CCSD theory seems to compensate for most of the MP2 effect on the barrier, i.e., there is a delicate balance between the δ [MP2] and δ [CCSD] increments.

TABLE III. Relativistic corrections to the inversion barrier of water.^a

| Basis | RHF | | | | | MP2 | | | | CCSD(T) | | | | |
|---------------|--------|------|------|--------|-------|--------|------|--------|-------|---------|------|------|--------|-------|
| | D1 | | D2 | MV | Sum | D1 | D2 | MV | Sum | D1 | | D2 | MV | Sum |
| | O | H | | | | | | | | O | H | | | |
| cc-pVTZ(58) | -156.6 | -1.7 | +2.6 | +211.1 | +55.4 | -163.4 | +2.6 | +219.9 | +59.1 | -163.7 | -1.6 | +3.0 | +222.4 | +60.1 |
| cc-pCVTZ(71) | -157.4 | -1.7 | +2.6 | +211.8 | +55.3 | -161.8 | +2.6 | +216.2 | +57.0 | -162.4 | -1.6 | +2.6 | +219.5 | +58.1 |
| cc-pVQZ(115) | -158.6 | -1.7 | +2.5 | +214.4 | +56.6 | -158.9 | +2.6 | +212.6 | +56.3 | -160.0 | -1.6 | +2.6 | +216.4 | +57.5 |
| cc-pCVQZ(144) | -157.6 | -1.7 | +2.5 | +211.8 | +55.0 | -158.7 | +2.5 | +211.6 | +55.4 | -159.7 | -1.6 | +2.5 | +215.2 | +56.4 |

^aObtained with all electrons correlated. All values are given in cm⁻¹. D1=one-electron Darwin term; D2=two-electron Darwin term; MV=one-electron mass-velocity term.

- (7) The performance of the CCSD(T) method, which perturbatively approximates contributions from connected triple excitations, is excellent, as judged from the small differences between the CCSD(T) and CCSDT results (n.b., the minuscule $\delta[\text{CCSDT}]$ increments in Table I).
- (8) There is excellent agreement among extrapolated CC, MP, and CI barrier heights. With the cc-pV(T/D)Z basis, the MP ∞ , CCSDT(Q), and full-CI (FCI) barrier heights are 11 726, 11 736, and 11 738 cm $^{-1}$, respectively. In our experience, higher-order correlation effects tend to diminish as the basis set is enlarged. Thus, all indications are that the correlation increments past CISDTQ are less than a few cm $^{-1}$ in the one-particle limit. These findings give special credence to the Series I results of the present study.

A theoretically sound approach to pinpointing *ab initio* limits is provided by explicitly correlated methods,^{35,51–56,58} which effectively deal with the electron-electron cusp problem by employing wave functions depending explicitly on interelectronic distances. Although the linear R12 methods surely have the potential to provide very accurate correlated total energies (within a few tenths of a mE $_h$), it nevertheless proved difficult here to obtain a highly accurate estimate of the barrier to linearity of water. It appears that uncertainties in total energies of a few tenths of a mE $_h$, are too large even if one moves on the same PES. These uncertainties are mainly due to the approximations involved in computing the many-electron integrals (with three electrons or more). The approximations^{35,58} consist of inserting the approximate resolution of the identity (RI) represented in the given one-electron basis, and they are seemingly not equally accurate for the bent and the linear structures of water. As a result, the errors due to the RI approximations are not well balanced with traditional basis sets, not even with the K1 and K2 basis sets, which had been designed specifically for R12 calculations. A balanced inclusion of the RI approximation is most critical when the Hamiltonian is decomposed into a many-electron Fock operator and a fluctuation potential, as is done in Møller–Plesset theory. Thus, at the R12 level, the MP2 calculations are particularly vulnerable to unbalanced RI approximations. The total coupled cluster results (with and without inclusion of triples) are much less sensitive. Indeed, the K1 CCSD(T)-R12/B result of 11 190 cm $^{-1}$ compares well with the K2 CCSD(T)-R12/B result of 11 221 cm $^{-1}$, as well as the conventional aug-cc-pV5Z and cc-pV6Z CCSD(T) results of 11 193 and 11 191 cm $^{-1}$, respectively.

One important conclusion of this study is that one can greatly improve the quality of R12 relative energy predictions in general and the convergence behavior of the barrier to linearity of water in particular by using precisely the same basis set for the calculations at the two reference structures. This is achieved by a procedure which one would traditionally term intramolecular counterpoise (ICP) correction.^{27(a)} Construction of the augmented basis set for the ICP calculations is done as follows. Consider the bisector of the O–H bonds fixed. Then, in going from the bent to the linear reference form, two hydrogens move. The calculations denoted +ICP in Table I utilized basis sets composed of the usual

basis sets augmented by basis functions on the ghost Hs centered on positions corresponding to the other reference form. While we do not think that the intramolecular counterpoise correction is of relevance for the larger basis sets employed in this study, it seems that a much more balanced treatment of the RI approximation results if the basis sets are the same by design during the two energy calculations of concern. The considerable scatter observed for the barrier height using smaller basis sets during R12 calculations (the results of which are not listed in Table I) reduces considerably for the ICP calculations. It must also be noted that the ICP correction has an enormous effect at the standard MP2 level. For example, using the K1 basis set, the MP2 correlation contribution changes from +13.0 to –254.3 cm $^{-1}$. One problem with the ICP scheme is, of course, numerical stability. The union of the two basis sets could result in an almost linearly dependent basis. Nevertheless, in the present, admittedly favorable, case no almost linearly dependent functions had to be discarded.

RHF energies obtained with correlation-consistent basis sets of increasing quality can be extrapolated^{6,26,59,60} to the complete basis set (CBS) limit using the exponential form

$$E_X = E_{\text{CBS}} + a \exp(-bX), \quad (1)$$

which effectively assumes that incremental cc-pVXZ \rightarrow cc-pV(X+1)Z lowerings of the total energy lie in a geometric progression. The extrapolated total energies, E_{CBS} , based on aug-cc-pV(Q,5,6)Z results are –76.067 35 E $_h$ and –76.016 10 E $_h$ at the bent and linear structures, respectively. These total energies are consistent with previous Hartree–Fock estimates,^{6,26,60} and yield a limiting value of 11 247 cm $^{-1}$ for the barrier.

The proper extrapolation of correlation energies is less clear. Several schemes have been proposed in the literature, almost all of which are based on analytic investigations of partial-wave expansions.^{61,62} In this work we follow the approach used in Ref. 26 and in the recent proposal of Halkier *et al.*,⁶³ whereby the CBS correlation energy is estimated by the simple formula

$$E_{\text{CBS}}(X, Y) = \frac{E^X X^3 - E^Y Y^3}{X^3 - Y^3}, \quad (2)$$

in which E^X and E^Y denote correlation energies obtained from correlation-consistent basis sets with cardinal numbers X and Y .

Application of Eq. (2) to the total correlation energies determined with the cc-pV5Z and cc-pV6Z basis sets at the conventional MP2, CCSD, and CCSD(T) levels of theory yields the following net barriers to linearity when the resulting $E_{\text{CBS}}(5,6)$ correlation components are appended to the extrapolated RHF limit of 11 247 cm $^{-1}$, ΔE_e {MP2, CCSD, CCSD(T)} = {10 876, 11 159, 11 137} cm $^{-1}$. The CBS MP2 barrier changes by only 1 cm $^{-1}$ if the extrapolation is performed instead with the aug-cc-pVXZ series, and it also agrees nicely with our earlier result of 10 864 cm $^{-1}$.²⁶ The corresponding K2+ICP R12/B barriers are ΔE_e {MP2, CCSD, CCSD(T)} = {10 899, 11 204, 11 187} cm $^{-1}$. Therefore, the R12 scheme predicts barriers which are {23, 45, 50} cm $^{-1}$ higher than those given by the conventional extrapolation.

tions. These disparities are disappointingly large, and we believe that they represent the level of imprecision inherent in *both* techniques for inferring one-particle limits. In essence, they indicate current limits of accuracy for predicting the water barrier by state-of-the-art *ab initio* methods. The conventional {RHF, MP2, CCSD, CCSD(T)} barriers at the CBS limit, obtained by extrapolating the relevant aug-cc-pV{T,Q5}Z+ICP results of Table I using Eqs. (1) and (2), are {11 246, 10 898, 11 181, 11 164} cm^{-1} . To extract a final valence focal-point result, we take the average of the three reported CBS CCSD(T) barriers, add a $+22 \text{ cm}^{-1}$ shift from Table I for connected quadruple excitations, and append error bars to span the extrapolation uncertainty. This procedure gives a vibrationless barrier of $11\,184 \pm 30 \text{ cm}^{-1}$. The corresponding value from Ref. 26, $11\,112 \text{ cm}^{-1}$, is slightly smaller, primarily because the $\delta[\text{CCSD}]$ increment therein could not be extrapolated to the CBS limit with the data available.

B. Core correlation

The origin of the core correlation effect on the inversion barrier of water is the rehybridization of lone pairs of electrons, resulting in changes in core penetration and radial correlation. In order to investigate core correlation, traditional basis sets designed to describe bonding involving valence electrons must be augmented with tight (high exponent) Gaussian functions able to describe the core region adequately.^{26,64–66} Such basis sets, denoted by cc-pCVXZ, have recently been designed by Dunning and co-workers,⁴⁶ and are employed in this study. The results for the contribution of core correlation to the inversion barrier of water are collected in Table II.

It is clear from Table II that the core correlation contribution to the water barrier is comparatively large, but not particularly sensitive to level of theory; neglecting the unreliable cc-pCVDZ numbers, the value of the correction scatters between -85 and -110 cm^{-1} . It is concluded that, at least in the present case, the estimate of core correlation obtained at the traditional MP2 level, where rather large molecular systems can be studied without undue effort, is sufficiently accurate. The comparison of cc-pCVQZ MP2 and K1/K2 MP2-R12/A results indicates that the inclusion of R12 coordinates in the core correlation treatment is not important in predicting the effect on the barrier, even at the level of precision sought in this study. The best extrapolated estimate of the core correlation correction to the barrier to linearity of water is -98 cm^{-1} , obtained by appending a cc-pCVQZ CCSD(T)–MP2 shift of $+11 \text{ cm}^{-1}$ to the K2 MP2-R12/A value.

C. Relativistic effects

In this study, relativistic corrections to the electronic energy have been gauged by a first-order perturbation theory approach applied to the mass-velocity (MV) and Darwin (D) terms.^{67,68} The one-electron MVD and the two-electron Darwin terms were calculated by a slight modification of the DIRCCR12 package³⁴ following the recipe of Ref. 68 for the determination of the two-electron Darwin term. Some of the

one-electron MVD calculations were checked against results obtained from the ACES II program package.^{26,30}

The results obtained at the RHF, MP2, and CCSD(T) levels of theory using basis sets of differing quality are given in Table III. A few aspects of these data warrant comment.

- (1) The exact solution of the Dirac equation⁶⁷ for the hydrogenic O^{7+} atom in its ground state yields an electronic energy of $-32.027 E_h$, as compared to $-32.000 E_h$ from the nonrelativistic Schrödinger equation. Therefore, the oxygen $1s$ core electrons are expected to give a relativistic correction of $2(-0.027) = -0.054 E_h$. The absolute magnitude of the relativistic correction determined in this study for water is $-0.055 E_h$, which is thus almost completely attributable to the $1s$ electrons of the oxygen atom.
- (2) The mass-velocity (MV) term corrects the kinetic energy of the system, and it is always negative. The one-electron Darwin (D1) term corrects the Coulomb attraction, and it always increases the total energy of the system. In agreement with this physical basis, the explicitly computed MV and D1 corrections are both substantial, about $0.2 E_h$, and they have opposite sign, canceling out most of their effect.
- (3) The two-electron Darwin (D2) correction term serves to reduce the repulsion between electrons; it is negative, and it is expected to be diminutive, since it depends on the minuscule probability of two electrons being at the same point in space. Calculations show that the D2 correction terms is indeed small, only $-0.003 E_h$. This two-electron contribution is not only petite but also virtually identical in the linear and bent structures, making its effect on the barrier almost negligible. Nevertheless, its magnitude is comparable to the electron correlation contribution to the relativistic effect.
- (4) The overall relativistic shift on the barrier is not particularly sensitive to the level of theory, all results lying between 55 and 60 cm^{-1} . Our computations also show that the shift is not affected by the addition of core polarization functions to the basis set.

Our final prediction from Table III is that relativistic effects increase the inversion barrier of water by $+58 \text{ cm}^{-1}$. Related work has shown that there is a slight but significant modulation of the relativistic correction over the PES in the vicinity of the equilibrium configuration.^{3,69} The modulation takes on a different sign upon stretching and bending of the molecule.³

D. The diagonal Born–Oppenheimer correction (DBOC)

Computation of the diagonal Born–Oppenheimer correction (DBOC) was performed at the Hartree–Fock level within the formalism of Handy, Yamaguchi, and Schaefer⁷⁰ and by means of the BORN program operating within the PSI package.³¹ As expected, the DBOC correction is small; it is -17 cm^{-1} at the DZP RHF level.²⁶

E. Net vibrationless barrier

In conclusion, our final prediction for the vibrationless inversion barrier of water is $(11\,184 - 98 + 58 - 17) = 11\,127\text{ cm}^{-1}$. This result is substantially higher than the value of $10\,966\text{ cm}^{-1}$, which was determined from the high-quality empirical PJT2 potential,² and almost the same as $11\,128\text{ cm}^{-1}$, which can be obtained from the analytical form of the semitheoretical PS potential.⁶ Given the insufficiency of the spectroscopic data near linearity, the apparent superiority of the PS barrier may be attributable mostly to improvement of the initial *ab initio* parameters in the surface fitting. Note, however, that the underlying theoretical part of the PS potential does not contain explicitly the substantial relativistic modulation determined here and elsewhere.³

III. ANHARMONIC FORCE FIELDS

Determination of the anharmonic force fields of water from the analytic potentials and from *ab initio* energy calculations followed well-established procedures.^{29,71,72} Evaluation of force constants via higher-order central-difference formulas (FINDIF) and through unweighted least-squares fitting (LSQ) utilized exactly the same set of energy values. The necessary single, double, and triple distortions can be described as $\{k, l, m\} \times \pm 0.02 (\text{\AA}, \text{rad})$, $\{k, l, m\} = 0, 1, 2, 3$ along the simple {stre, stre, bend} internal coordinates. Energy points have been computed at the all-electron aug-cc-pCVTZ CCSD(T) level as well as from the PJT2 (Ref. 2) and PS (Ref. 6) potentials. The reference geometries employed for the *ab initio* computations are the same as those used for the focal-point analysis; therefore, they are not precisely stationary points at the level of theory applied. Considerations for dealing with the resulting residual gradients have been extensively developed by Allen and Császár.⁷³ Relativistic corrections to the electronic energies were obtained by means of first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms (*vide supra*), as implemented in ACESII.³⁰ The FINDIF and LSQ force constants corresponding to the bent and linear structures are reported in Tables IV and V, respectively. The standard errors of the least-squares fit, given in these tables next to the force constants, provide an estimate of the accuracy of the constants determined.

We note here only one physically significant feature of the force fields; the stretching force constants f^{rr} , f^{rrr} , and f^{rrrr} at the linear geometry are considerably larger than their equilibrium counterparts. This is fully in line with the observed shortening of the O–H distance upon opening of the bond angle. This observation can be explained by noting that O–H bonds in the linear structure are nominally⁷⁴ formed from *sp* rather than *sp*³ hybrids. In accord with Bent's rules,⁷⁵ the increased *s* character should result in stronger and thus shorter bonds.

In order to judge the quality of the analytical PJT2 (Ref. 2) and PS (Ref. 6) PESs of water an attempt was made to determine full sextic force fields corresponding to the analytical potentials at their respective bent (C_{2v}) and linear ($D_{\infty h}$) stationary points. It turned out that many of the quintic and sextic force constants are undetermined (unphysical)

in the PJT2 force field as the corresponding terms have not been included in the construction of this empirical potential. These fields were compared with high-quality *ab initio* force fields determined as part of this study or taken from the literature.³ The agreement between the *ab initio* and the PJT2 and PS force fields for the C_{2v} geometry is quite satisfactory (see Table IV), but only through the quartic level. We highlight only those coupling force constants in the quartic field for which the *ab initio* and the empirical/semitheoretical data do not agree with each other within a factor of 2. There is general agreement for the cubic force constants, with the exception of $f^{rr\alpha}$. It is noteworthy in this case that early empirical quartic force field studies¹⁴ obtained a value of $+0.4\text{ aJ \AA}^{-2}\text{ rad}^{-1}$ for $f^{rr\alpha}$. For some of the quartic force constants ($f^{rrr'r'}$, $f^{rrrr'}$, $f^{rrr'\alpha}$) the discrepancies are quite noticeable. All available *ab initio* results indicate that $f^{rrr'r'}$ has a small negative value, whereas the PJT2 force field gives a positive value. Similarly, the large negative value obtained from the PJT2 PES for $f^{rrr'\alpha}$ is not supported by the *ab initio* results. The discrepancies between the force fields at the linear geometry of water are considerably larger (see Table V). Such comparisons test the ability of the PJT2 and PS surfaces to accurately extrapolate to the fully linear regime. Therefore, the most important origin of the discrepancies observed is that during the construction of the empirical PJT2 potential there were no observations available for vibrational states fixing the value of these constants. For these constants, the *ab initio* values are believed to be more accurate. This view is further supported by the much better agreement between the present *ab initio* constants and those derived from the semitheoretical PS potential. This study proves again^{64,71(c)} how difficult it is to determine, from experimental data alone, reliable, physically relevant higher-order force constants, especially the quintic and sextic terms of the potential energy expansion, which make diminutive contributions to the energy values.

It is clear from Tables IV and V that the relativistic correction to the PES of water has only a marginal effect on the geometric derivatives (force fields) of the PES at any given point. Deviations between nonrelativistic and "relativistic" force constants are always less than 1%. Nevertheless, it should be noted that (a) even such small corrections can result in a change of $1\text{--}2\text{ cm}^{-1}$ in the calculated fundamental frequencies, as can also be shown easily for diatomic species; and (b) in the case of the global PES of water, relativistic corrections to the PES can be as much as 200 cm^{-1} ,^{3,26} and the resulting vibrational correction can approach $10\text{--}15\text{ cm}^{-1}$ for excited vibrational levels some $20\,000\text{ cm}^{-1}$ above the minimum.³

PJT2 force constants have been determined not only for the PJT2 stationary points, but also at the *ab initio* reference geometries chosen for this study. Somewhat unexpectedly,⁷³ this shift in the reference structure does not further improve the remarkable agreement between the present purely *ab initio* and the empirical PJT2 force constants.

Once a force field representation of the potential is available, spectroscopic constants, vibrational energy levels, and zero-point vibrational energy (ZPVE) corrections can be ob-

TABLE IV. Anharmonic force constants for the electronic ground state of water at its bent (C_{2v}) equilibrium geometry.^a

| Term | aug-cc-pCVTZ CCSD(T) ^{b,c} | | aug-cc-pCVTZ CCSD(T)+REL ^b | PJT2 ^d | PJT2 ^b | PS ^e |
|--------------------------------------|-------------------------------------|--------------|--|-------------------|-------------------|-----------------|
| | FINDIF | LSQ | | | | |
| f^r | -0.014 103 8 | -0.014 103 8 | -0.014 100 0 | 0.000 0 | -0.007 0 | 0.000 0 |
| f^α | -0.000 052 | -0.000 052 | 0.000 710 | 0.000 0 | -0.001 4 | 0.000 0 |
| f^{rr} | 8.468 51 | 8.468 52(2) | 8.458 | 8.447 | 8.394 | 8.460 |
| $f^{rr'}$ | -0.096 55 | -0.096 55(1) | -0.097 70 | -0.102 | -0.100 | -0.103 |
| $f^{r\alpha}$ | 0.258 40 | 0.258 40(1) | 0.258 5 | 0.263 | 0.264 | 0.258 |
| $f^{\alpha\alpha}$ | 0.700 495 | 0.700 49(1) | 0.700 54 | 0.704 | 0.705 | 0.703 |
| f^{rrr} | -58.572 4 | -58.571 1(5) | -58.515 6 | -56.37 | -56.37 | -58.73 |
| $f^{rrr'}$ | -0.063 8 | -0.062 1(1) | -0.061 9 | -0.276 | -0.266 | -0.069 |
| $f^{rr\alpha}$ | -0.112 6 | -0.111 8(1) | -0.115 5 | -0.059 | -0.060 | -0.107 |
| $f^{rr'\alpha}$ | -0.499 1 | -0.498 4(2) | -0.500 1 | -0.189 | -0.572 | -0.515 |
| $f^{r\alpha\alpha}$ | -0.302 8 | -0.301 8(1) | -0.302 5 | -0.309 | -0.317 | -0.319 |
| $f^{\alpha\alpha\alpha}$ | -0.680 2 | -0.679 7(5) | -0.680 0 | -0.751 | -0.746 | -0.705 |
| f^{rrrr} | 366.6 | 366.6(1) | 366.4 | 320.3 | 317.8 | 366.6 |
| $f^{rrrr'}$ | -0.65 | -0.64(3) | -0.64 | 1.62 | 1.48 | -0.67 |
| $f^{rrr'r'}$ | 0.18 | 0.17(1) | 0.17 | 1.73 | 1.64 | 0.44 |
| $f^{rrr\alpha}$ | -1.51 | -1.51(2) | -1.51 | -2.37 | -2.34 | -1.49 |
| $f^{rrr'\alpha}$ | 0.46 | 0.23(4) | 0.46 | -6.16 | -6.06 | -4.25 |
| $f^{rr\alpha\alpha}$ | -0.207 | -0.259(5) | -0.216 | -0.70 | -0.69 | -0.32 |
| $f^{rr'\alpha\alpha}$ | 0.55 | 0.55(17) | 0.55 | 0.15 | 0.43 | 0.69 |
| $f^{r\alpha\alpha\alpha}$ | 0.71 | 0.71(2) | 0.72 | 1.30 | 1.30 | 0.72 |
| $f^{\alpha\alpha\alpha\alpha}$ | -0.62 | -0.61(12) | -0.62 | -0.640 | -0.651 | -0.757 |
| f^{rrrrr} | -2 429.1 | | | -2 863.9 | | -2 549.9 |
| $f^{rrrrr'}$ | 3.89 | | | 0.24 | | 11.0 |
| $f^{rrrr'r'}$ | 2.66 | | | -6.1 | | 5.9 |
| $f^{rrrr\alpha}$ | 0.82 | | | 17.5 | | 1.6 |
| $f^{rr\alpha\alpha\alpha}$ | -1.36 | | | | | -0.5 |
| $f^{\alpha\alpha\alpha\alpha}$ | -3.41 | | | 4.20 | | -2.0 |
| f^{rrrrrr} | 16 856 | | | 25 976 | | 8 644 |
| $f^{rrrrrr'}$ | -56.1 | | | -73.4 | | -0.8 |
| $f^{rrrrr'r'}$ | -20.7 | | | 5.0 | | -89.1 |
| $f^{rrrrr'\alpha}$ | -44.3 | | | 12.3 | | 2.4 |
| $f^{rrrr\alpha\alpha}$ | -20.5 | | | -3.0 | | 41.4 |
| $f^{\alpha\alpha\alpha\alpha\alpha}$ | -18.3 | | | 7.3 | | 9.7 |

^aUnits of the force constants are consistent with energy measured in aJ, distances in Å, and angles in rad. The *ab initio* quintic and sextic constants are taken from Ref. 3 (set I of Table III) and correspond to a different reference structure. REL=relativistic correction, the energy corrections were obtained by means of first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms.

^bFor $\{r, \alpha\} = \{0.958 85 \text{ \AA}, 104.343^\circ\}$ corresponding to the all-electron aug-cc-pVTZ CCSD(T) equilibrium structure (Ref. 26).

^cFINDIF=force constants determined through the use of finite-difference formulas. LSQ=force constants determined through the use of unweighted linear least-squares fitting. In both procedures altogether 37 energy values have been utilized. In the case of LSQ, values given in parentheses refer to standard errors of the fit in the last digit(s) given.

^dFor $\{r, \alpha\} = \{0.957 92 \text{ \AA}, 104.500^\circ\}$ corresponding to the equilibrium of the PJT2 potential (Ref. 2).

^eFor $\{r, \alpha\} = \{0.957 84 \text{ \AA}, 104.508^\circ\}$ corresponding to the equilibrium of the PS potential (Ref. 6).

tained through variational, perturbational, or mixed procedures. Effective barriers may play a special role, as in the case of the HCN–HNC rearrangement.⁷⁶ In this work both direct second-order vibrational perturbation theory (VPT2) (Ref. 77) and a mixed procedure, the nonrigid-rotation-large-amplitude-internal-motion Hamiltonian (NRLH) method of Szalay,⁷⁸ were applied. The required force field transformations between curvilinear internal and rectilinear Cartesian coordinate spaces, up to fourth order, were performed analytically and utilized the program INTDER95.^{73,79} The VPT2 calculations were performed, both at the equilibrium and at the linear geometry, by the program package SPECTRO.⁸⁰

The correction to the barrier to linearity of water due to

zero-point vibrations can be calculated using either harmonic or anharmonic frequencies. Excluding the bending frequency, the harmonic corrections range from +350 to +359 cm^{-1} for the *ab initio* potentials. The PS value is rather similar at +367 cm^{-1} . The PJT2 value at +234 cm^{-1} is, however, much smaller. The *ab initio* anharmonic correction values, in the space of the two stretching vibrations, are between +2.6 and +3.1 cm^{-1} , while the PS value is +5.5 cm^{-1} . The empirical PJT2 potential gives again a substantially different value, around -5 cm^{-1} .

The NRLH method,⁷⁸ as applied to H₂O, amounts to an adiabatic separation of the bending and stretching motions. The bending is described by a geometrically defined curvi-

TABLE V. Anharmonic force constants for the electronic ground state of water at the linear ($D_{\infty h}$) geometry.^a

| Term | aug-cc-pCVTZ CCSD(T) ^{b,c} | | aug-cc-pCVTZ CCSD(T)+REL ^b | PJT2 ^d | PJT2 ^b | PS ^e |
|--------------------------------------|-------------------------------------|--------------|--|-------------------|-------------------|-----------------|
| | FINDIF | LSQ | | | | |
| f^r | -0.013 26 | -0.013 26 | -0.012 03 | 0.000 0 | 0.057 7 | 0.000 0 |
| f^{rr} | 10.128 32 | 10.128 32(2) | 10.115 1 | 9.88 | 9.43 | 10.12 |
| $f^{rr'}$ | -0.342 81 | -0.342 81(1) | -0.344 4 | -0.395 | -0.434 | -0.342 |
| $f^{\alpha\alpha}$ | -0.660 80 | -0.660 80(2) | -0.663 61 | -0.587 | -0.595 | -0.652 |
| f^{rrr} | -69.044 8 | -69.047 4(5) | -68.983 1 | -69.68 | -66.62 | -69.25 |
| $f^{rrr'}$ | 0.185 4 | 0.184 4(1) | 0.183 9 | -3.34 | -2.96 | 0.137 |
| $f^{r\alpha\alpha}$ | -0.557 5 | -0.559 0(2) | -0.563 0 | -0.647 | -0.633 | -0.540 |
| f^{rrrr} | 435.5 | 435.6(1) | 435.4 | 459.1 | 426.4 | 432.1 |
| $f^{rrrr'}$ | -0.96 | -0.94(4) | -0.98 | 45.8 | 42.6 | -0.17 |
| $f^{rrr'r'}$ | -2.09 | -2.01(1) | -2.09 | 13.8 | 12.6 | -1.36 |
| $f^{rr\alpha\alpha}$ | -1.34 | -1.34(1) | -1.34 | 1.73 | 1.68 | -1.43 |
| $f^{rr'\alpha\alpha}$ | -0.31 | -0.24(20) | -0.30 | 0.50 | 0.52 | -0.31 |
| $f^{\alpha\alpha\alpha\alpha}$ | 4.73 | 4.71(13) | 4.76 | 2.06 | 2.29 | 4.69 |
| f^{rrrrr} | -3 020.3 | | -3 020.1 | -5 580 | | -3074 |
| $f^{rrrrr'}$ | 21 987 | | 21 957 | 53 609 | | 11 059 |
| $f^{\alpha\alpha\alpha\alpha\alpha}$ | .. ^f | | .. ^f | 39.9 | | -34.2 |

^aUnits of the force constants are consistent with energy measured in aJ, distances in Å, and angles in rad. REL=relativistic correction, the energy corrections were obtained by means of first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms.

^bFor $r = 0.934 11$ Å corresponding to the all-electron aug-cc-pVTZ CCSD(T) equilibrium structure (Ref. 26).

^cFINDIF=force constants determined through the use of finite-difference formulas. LSQ=force constants determined through the use of unweighted linear least-squares fitting. In both procedures altogether 27 energy values have been utilized. In the case of LSQ, values given in parentheses refer to standard errors of the fit in the last digit(s) given.

^dFor $r = 0.927 87$ Å corresponding to the equilibrium of the PJT2 potential (Ref. 2).

^eFor $r = 0.933 5$ Å corresponding to the equilibrium of the PS potential (Ref. 6).

^fIt is not possible to determine this force constant from our *ab initio* energy points.

linear coordinate, while rectilinear displacement coordinates, in the present case normal coordinates, describe the stretching motions. The effect of stretching vibrations on the bending motion is taken into account by second-order perturbation theory. This results in an effective bending potential and an effective bending Hamiltonian. Values of the effective bending potential, in the ground stretching vibrational state, were determined for the C_{2v} and $D_{\infty h}$ reference structures, utilizing the force fields and geometries given in Tables IV and V, respectively. The vibrational contribution to the barrier to linearity can be obtained by subtracting the value of the effective bending potential calculated at the bent equilibrium structure from that calculated at the linear configuration. The correction originating exclusively from the bending dependence of the harmonic stretching frequencies can be calculated similarly and it appears to account for almost all of the vibrational correction. The {aug-cc-pCVTZ CCSD(T), aug-cc-pCVTZ CCSD(T)+REL, PJT2, PS} zero-point vibrational energy contributions to the barrier are {352, 354, 312, 368} cm^{-1} . The PJT2 correction deviates again substantially from the other values.

The zero-point vibrational corrections obtained using the VPT2 and NRLH approaches are distinct due to some important differences between the two methods. In particular, NRLH employs a curvilinear, geometrically defined bending coordinate and ensures that the Sayvetz condition is satisfied. This results in an efficient separation of the large-amplitude bending and the small-amplitude stretching vibrations. A manifestation of the efficiency of this separation is that the

NRLH anharmonicity parameters, not reported here, satisfy relations derived from local modes theory⁸¹ very well.

IV. CONCLUSIONS

The following conclusions can be drawn from the numerous results presented in this study:

- (1) The extrapolated RHF barrier of water is $11\,247 \pm 2 \text{ cm}^{-1}$. The extrapolated CCSD and CCSD(T) energy increments differ somewhat based on which electronic energy results are employed for the extrapolation procedure. CCSD-R12 and CCSD(T)-R12 computations seem to converge to the limiting value for the barrier from above, while conventional calculations converge from below. Adding $+22 \text{ cm}^{-1}$ for the effect of higher (quadruple) excitations, we obtain $11\,184 \text{ cm}^{-1}$ for the extrapolated valence-only barrier height of water. A conservative error estimate for this calculated barrier height is $\pm 30 \text{ cm}^{-1}$. This error estimate is surprisingly large when compared to the effort devoted to the computation of the barrier and is clearly attributable to the slow basis set convergence at correlated levels of *ab initio* theory. According to our extrapolation formulas, it is necessary to proceed through the $X = 10$ level (1276 functions) of the cc-pVXZ basis set series to converge conventional, correlated evaluations of the barrier to within 10 cm^{-1} .
- (2) Introducing exactly the same basis set and thus the same resolution of the identity in computations for the bent and the linear references, one can improve considerably

the quality of explicitly correlated R12 relative energies and the convergence behavior of the resulting energy values. Traditionally, one would term the procedure employed intramolecular counterpoise (ICP) correction.

- (3) The core correlation contribution to the barrier, resulting from changes in core penetration and radial correlation due to rehybridization of lone pairs of electrons, is relatively large, about -98 cm^{-1} . The inclusion of R12 coordinates in the core correlation treatment does not seem to be important in predicting the effect on the barrier.
- (4) The relativistic energy correction of water comes almost exclusively from the oxygen $1s$ core orbital; its value is $-0.055 E_h$. The individual mass-velocity (MV) and one-electron Darwin (D1) corrections are both substantial, about $0.2 E_h$, and they have opposite sign, canceling out most of their effect. The two-electron Darwin (D2) correction term is small, only $-0.003 E_h$. This two-electron contribution is not only petite but also virtually identical in the linear and bent structures, making its effect on the barrier almost negligible. Nevertheless, the magnitude of the D2 term is comparable to the electron correlation contribution to the relativistic effect. Overall, the relativistic effects increase the inversion barrier of water by $+58 \text{ cm}^{-1}$.
- (5) Taking -17 cm^{-1} for the diagonal Born–Oppenheimer correction (DBOC), obtained from a DZP RHF calculation, our final prediction for the vibrationless inversion barrier of water is $(11\,184 - 98 + 58 - 17) = 11\,127 \text{ cm}^{-1}$. This value is substantially higher than the extrapolated barrier of $10\,966 \text{ cm}^{-1}$ determined from the high-quality empirical PJT2 potential. On the other hand, the best currently available full surface of Partridge and Schwenke displays a barrier ($11\,128 \text{ cm}^{-1}$) which is virtually identical to that obtained here, an occurrence which bodes well for its continued use.
- (6) Agreement between the *ab initio* force fields determined here and the PJT2 and PS force field representations of the respective surfaces for the bent equilibrium geometry is quite satisfactory, but only through the quartic level. For the force constants at the linear reference geometry the present *ab initio* values are believed to be more accurate than those derived from the PS and especially from the PJT2 hypersurfaces.

ACKNOWLEDGMENTS

The work of G.T. and A.G.Cs. has been partially supported by the Hungarian Ministry of Culture and Education (MKM/517 and FKFP 0117/1997) and by the Scientific Research Foundation of Hungary (OTKA T024044). The work of V.S. has been supported by the Scientific Research Foundation of Hungary (OTKA T25103) and by the Australian Research Council Large Grant Scheme (A29701390) administered by Dr. Sean Smith. A.G.C. and W.K. acknowledge partial support from the Departments of Chemistry and International Relations of the University of Oslo and grants NN2694K and NN2794K of the Norwegian Research Council. The research at the Center for Computational Quantum Chemistry at the University of Georgia was supported by the

U.S. Department of Energy, Office of Basic Energy Sciences, Fundamental Interactions Branch, Grant No. DE-FG02-97-ER14748. The help of Matt Leininger with the FCI calculations is gratefully acknowledged. Finally, the authors would like to thank Professor J. Tennyson, M. Quack, and Dr. O. Polyansky for helpful discussions.

- ¹N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, and J. Tennyson, *Chem. Phys. Lett.* **260**, 381 (1996).
- ²O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **105**, 6490 (1996).
- ³A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, *Chem. Phys. Lett.* **293**, 317 (1998).
- ⁴O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, and L. Wallace, *Science* **277**, 346 (1997).
- ⁵J. H. Schryber, O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Mol. Spectrosc.* **185**, 234 (1997).
- ⁶H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997).
- ⁷G. J. Harris, S. Viti, H. Y. Mussa, and J. Tennyson, *J. Chem. Phys.* **109**, 7197 (1998).
- ⁸O. L. Polyansky, N. F. Zobov, J. Tennyson, J. A. Lotoski, and P. F. Bernath, *J. Mol. Spectrosc.* **184**, 35 (1997).
- ⁹O. N. Ulenikov and G. A. Ushakova, *J. Mol. Spectrosc.* **117**, 195 (1986).
- ¹⁰(a) L. Wallace, P. Bernath, W. Livingstone, K. Hinkle, J. Busler, B. Gou, and K. Zhang, *Science* **268**, 1155 (1995); (b) T. Oka, *ibid.* **277**, 328 (1997).
- ¹¹T. Tsuji, *Annu. Rev. Astron. Astrophys.* **24**, 89 (1986).
- ¹²A. R. Hoy, I. M. Mills, and G. Strey, *Mol. Phys.* **24**, 1265 (1972).
- ¹³A. G. Császár and I. M. Mills, *Spectrochim. Acta A* **53**, 1101 (1996).
- ¹⁴G. S. Kedziora and I. Shavitt, *J. Chem. Phys.* **106**, 8733 (1997).
- ¹⁵S. Carter and N. C. Handy, *J. Chem. Phys.* **87**, 4294 (1987).
- ¹⁶(a) O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **101**, 7651 (1994); (b) C. D. Paulse and J. Tennyson, *J. Mol. Spectrosc.* **168**, 271 (1994); (c) O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, and L. Wallace, *ibid.* **186**, 422 (1997).
- ¹⁷P. Jensen, *J. Mol. Spectrosc.* **133**, 438 (1989).
- ¹⁸L. Halonen and T. Carrington, Jr., *J. Chem. Phys.* **88**, 4171 (1988).
- ¹⁹Z. Bačić, D. Watt, and J. C. Light, *J. Chem. Phys.* **89**, 947 (1988).
- ²⁰R. J. Bartlett, S. J. Cole, G. D. Purvis, W. C. Ermler, H. C. Hsieh, and I. Shavitt, *J. Chem. Phys.* **87**, 6579 (1987).
- ²¹I. M. Mills, in *Specialist Periodical Reports, Theoretical Chemistry*, edited by R. N. Dixon (The Chemical Society, London, 1974), Vol. 1.
- ²²R. Beardsworth, P. R. Bunker, P. Jensen, and W. P. Kraemer, *J. Mol. Spectrosc.* **118**, 50 (1986).
- ²³P. R. Bunker, P. Jensen, W. P. Kraemer, and R. Beardsworth, *J. Chem. Phys.* **85**, 3724 (1986).
- ²⁴Y. Guan and C. R. Quade, *J. Chem. Phys.* **86**, 4808 (1987).
- ²⁵G. J. Sexton and N. C. Handy, *Mol. Phys.* **51**, 1321 (1984).
- ²⁶A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108**, 9751 (1998).
- ²⁷(a) F. Jensen, *Chem. Phys. Lett.* **261**, 633 (1996); (b) J. S. Lee, *J. Phys. Chem. A* **101**, 8762 (1997).
- ²⁸(a) A. L. L. East and W. D. Allen, *J. Chem. Phys.* **99**, 4638 (1993); (b) W. D. Allen, A. L. L. East, and A. G. Császár, in *Structures and Conformations of Non-Rigid Molecules*, edited by J. Laane, M. Dakkouri, B. van der Veken, and H. Oberhammer (Kluwer, Dordrecht, 1993); (c) B. D. Wladkowski, W. D. Allen, and J. I. Brauman, *J. Phys. Chem.* **98**, 13532 (1994).
- ²⁹A. G. Császár, *Anharmonic Molecular Force Fields, in The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollmann, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998).
- ³⁰J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, *Int. J. Quantum Chem., Quantum Chem. Symp.* **26**, 897 (1992).
- ³¹C. L. Janssen, E. T. Seidl, G. E. Scuseria, T. P. Hamilton, Y. Yamaguchi, R. B. Remington, Y. Xie, G. Vacek, C. D. Sherrill, T. D. Crawford, J. T. Fermann, W. D. Allen, B. R. Brooks, G. B. Fitzgerald, D. J. Fox, J. F. Gaw, N. C. Handy, W. D. Laidig, T. J. Lee, R. M. Pitzer, J. E. Rice, P. Saxe, A. C. Scheiner, and H. F. Schaefer III, *psi 2.0.8*, PSITECH Inc., Watkinsville, Georgia, 1994.
- ³²M. J. Frisch *et al.*, GAUSSIAN 94, Revision B.2, Gaussian, Inc., Pittsburgh, Pennsylvania, 1995.
- ³³SORE program, second-order r_{12} energy, written by W. Klopper.

- ³⁴(a) DIRCCR12 program, written by J. Noga and W. Klopper; (b) W. Klopper and J. Noga, *J. Chem. Phys.* **103**, 6127 (1995).
- ³⁵W. Klopper, r_{12} *Dependent Wave Functions*, in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollmann, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998).
- ³⁶(a) C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951); (b) W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, New York, 1986).
- ³⁷(a) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Symp.* **10**, 1 (1976); (b) R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980); (c) K. Raghavachari, J. A. Pople, E. S. Replogle, and M. Head-Gordon, *J. Phys. Chem.* **94**, 5579 (1990).
- ³⁸R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- ³⁹(a) G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer III, *J. Chem. Phys.* **86**, 2881 (1987); (b) A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, *ibid.* **87**, 5361 (1987).
- ⁴⁰(a) J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987); (b) G. E. Scuseria and H. F. Schaefer III, *Chem. Phys. Lett.* **152**, 382 (1988).
- ⁴¹I. Shavitt, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977).
- ⁴²(a) K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989); (b) G. E. Scuseria and T. J. Lee, *J. Chem. Phys.* **93**, 5851 (1990).
- ⁴³N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari, and G. W. Trucks, *Chem. Phys. Lett.* **164**, 185 (1989).
- ⁴⁴C. E. Dykstra, *Chem. Phys. Lett.* **45**, 466 (1977).
- ⁴⁵(a) O. Goscinski, *Int. J. Quantum Chem.* **1**, 769 (1967); (b) N. C. Handy, P. J. Knowles, and K. Somasundram, *Theor. Chim. Acta* **68**, 87 (1985); (c) W. D. Laidig, G. Fitzgerald, and R. J. Bartlett, *Chem. Phys. Lett.* **113**, 151 (1985).
- ⁴⁶T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); D. E. Woon and T. H. Dunning, Jr., *ibid.* **98**, 1358 (1993); **100**, 2975 (1994); **103**, 4572 (1995); A. K. Wilson, T. v. Mourik, and T. H. Dunning, Jr., *J. Mol. Struct., THEOCHEM* **388**, 339 (1997).
- ⁴⁷Program DETCI, written by C. D. Sherrill and M. L. Leininger.
- ⁴⁸(a) V. Bakken, T. Helgaker, W. Klopper, and K. Ruud, *Mol. Phys.* **96**, 653 (1999); (b) see Table IX of W. Klopper, *J. Chem. Phys.* **102**, 6168 (1995).
- ⁴⁹*Structure Data of Free Polyatomic Molecules*, edited by K. Kuchitsu (Springer, Berlin, 1995), Vol. 23.
- ⁵⁰I. M. B. Nielsen, W. D. Allen, A. G. Császár, and H. F. Schaefer III, *J. Chem. Phys.* **107**, 1195 (1997).
- ⁵¹W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).
- ⁵²J. Noga and W. Kutzelnigg, *J. Chem. Phys.* **101**, 7738 (1994).
- ⁵³W. Klopper and J. Noga, *J. Chem. Phys.* **103**, 6127 (1995).
- ⁵⁴R. J. Gdanitz, *Chem. Phys. Lett.* **210**, 253 (1993).
- ⁵⁵R. Bukowski, B. Jeziorski, S. Rybak, and K. Szalewicz, *J. Chem. Phys.* **102**, 888 (1995).
- ⁵⁶H. F. King, *J. Chem. Phys.* **46**, 705 (1967).
- ⁵⁷J. Olsen, O. Christiansen, H. Koch, and P. Jørgensen, *J. Chem. Phys.* **105**, 5082 (1996).
- ⁵⁸W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).
- ⁵⁹D. Feller, *J. Chem. Phys.* **96**, 6104 (1992); **98**, 7059 (1993).
- ⁶⁰T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ⁶¹(a) C. Schwartz, *Phys. Rev.* **126**, 1015 (1962); (b) D. P. Carroll, H. J. Silverstone, and R. M. Metzger, *J. Chem. Phys.* **71**, 4142 (1979).
- ⁶²R. N. Hill, *J. Chem. Phys.* **83**, 1173 (1985).
- ⁶³A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- ⁶⁴A. G. Császár, *J. Phys. Chem.* **98**, 8823 (1994).
- ⁶⁵J. M. L. Martin and P. R. Taylor, *Chem. Phys. Lett.* **225**, 473 (1994).
- ⁶⁶A. G. Császár and W. D. Allen, *J. Chem. Phys.* **104**, 2746 (1996).
- ⁶⁷K. Balasubramanian, *Relativistic Effects in Chemistry, Part A: Theory and Techniques* (Wiley, New York, 1997).
- ⁶⁸W. Klopper, *J. Comput. Chem.* **18**, 20 (1997).
- ⁶⁹H. M. Quiney, H. Skaane, and I. P. Grant, *Chem. Phys. Lett.* **290**, 473 (1998).
- ⁷⁰N. C. Handy, Y. Yamaguchi, and H. F. Schaefer III, *J. Chem. Phys.* **84**, 4481 (1986).
- ⁷¹(a) J. K. G. Watson, *J. Mol. Spectrosc.* **41**, 229 (1972); (b) X-F. Zhou and P. Pulay, *J. Comput. Chem.* **10**, 935 (1989); (c) A. G. Császár, *J. Phys. Chem.* **96**, 7898 (1992).
- ⁷²C. Lanczos, *Applied Analysis* (Prentice-Hall, Englewood Cliffs, 1956).
- ⁷³W. D. Allen and A. G. Császár, *J. Chem. Phys.* **98**, 2983 (1993).
- ⁷⁴J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980). This paper provides a firm physical basis for determining a unique set of atomic hybrids and bond orbitals in a given molecule. The resulting "natural hybrid orbitals" are often substantially different from the classic "nominal" hybrids, but in the case of H₂O the essential trends in $\%(s,p)$ character upon bending are retained.
- ⁷⁵H. A. Bent, *Chem. Rev.* **61**, 275 (1961).
- ⁷⁶Z. Bačić and J. C. Light, *J. Chem. Phys.* **86**, 3065 (1987).
- ⁷⁷(a) H. H. Nielsen, *Rev. Mod. Phys.* **23**, 90 (1951); (b) D. Papoušek and M. R. Aliev, *Molecular Rotational-Vibrational Spectra* (Elsevier, Amsterdam, 1982); (c) D. A. Clabo, Jr., W. D. Allen, R. B. Remington, Y. Yamaguchi, and H. F. Schaefer III, *Chem. Phys.* **123**, 187 (1988); (d) W. D. Allen, Y. Yamaguchi, A. G. Császár, D. A. Clabo, Jr., R. B. Remington, and H. F. Schaefer, III, *ibid.* **145**, 427 (1990).
- ⁷⁸(a) V. Szalay, *J. Mol. Spectrosc.* **128**, 24 (1988); *J. Chem. Phys.* **92**, 3633 (1990).
- ⁷⁹INTDER is a set of programs written by W. D. Allen and co-workers which performs various vibrational analysis and higher-order nonlinear transformations among force field representations.
- ⁸⁰A. Willetts, J. F. Gaw, W. H. Green, Jr., and N. C. Handy, SPECTRO, a second-order rovibrational perturbation theory program, version 3.0, University Chemical Laboratory, Cambridge, United Kingdom, 1994.
- ⁸¹(a) I. M. Mills and A. G. Robiette, *Mol. Phys.* **56**, 743 (1985); (b) R. G. Della Valle, *ibid.* **63**, 611 (1988).