

Hyperpolarizability of H₂O revisited: accurate estimate of the basis set limit and the size of electron correlation effects

George Maroulis *

Department of Chemistry, University of Patras, GR-26500 Patras, Greece

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Abstract

A large (18s 13p 8d 5f / 12s 7p 3d 2f) basis set consisting of 256 uncontracted gaussian-type functions is expected to yield values near the Hartree–Fock limit for the static hyperpolarizability of H₂O: $\beta_{zxx} = -9.40$, $\beta_{zyy} = -1.35$, $\beta_{zzz} = -7.71$ and $\bar{\beta} = -11.07$ for $\beta_{\alpha\beta\gamma}$ ($e^3 a_0^3 E_h^{-2}$) and $\gamma_{xxxx} = 569$, $\gamma_{yyyy} = 1422$, $\gamma_{zzzz} = 907$, $\gamma_{xxyy} = 338$, $\gamma_{yyzz} = 389$, $\gamma_{zzxx} = 287$ and $\bar{\gamma} = 985$ for $\gamma_{\alpha\beta\gamma\delta}$ ($e^4 a_0^4 E_h^{-3}$) at the experimental equilibrium geometry (with z as the C₂ axis, molecule on the xz plane). The respective electron correlation corrections obtained with the single, double and perturbatively linked triple excitations coupled-cluster method and a [9s 6p 6d 3f / 6s 4p 2d 1f] basis set are $\beta_{zxx} = -0.45$, $\beta_{zyy} = -4.19$, $\beta_{zzz} = -6.09$, $\bar{\beta} = -6.44$ and $\gamma_{xxxx} = 267$, $\gamma_{yyyy} = 1228$, $\gamma_{zzzz} = 574$, $\gamma_{xxyy} = 295$, $\gamma_{yyzz} = 322$, $\gamma_{zzxx} = 152$, $\bar{\gamma} = 721$. For the static limit we propose $\bar{\beta} = -17.5 \pm 0.3 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = (171 \pm 6) \times 10^1 e^4 a_0^4 E_h^{-3}$, in near agreement with the experimental findings of $\bar{\beta} = -19.2 \pm 0.9 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = 1800 \pm 150 e^4 a_0^4 E_h^{-3}$ deduced from EFISH measurements at 1064 nm by Kaatz et al. [P. Kaatz, E.A. Donley, D.P. Shelton, J. Chem. Phys. 108 (1998) 849]. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The electric properties of water are a subject of considerable interest. Since our previous work on the hyperpolarizability of this molecule [1] important experimental and theoretical studies have enriched the field with new data. An accurate equilibrium dipole moment was determined by Shostak et al. [2] from molecular beam electric resonance spectroscopy (MBER). Recently, Kaatz et al. [3] reported first (β) and second ($\bar{\gamma}$) electric hyperpolarizability values extracted from gas-phase electric field induced second harmonic generation (EFISH) measurements. A number of important theoretical studies on the hyperpolarizability of water [4–10] brought forth various inconsistencies concerning either the convergence of the static values of these properties to the Hartree–Fock limit or the true size of the electron correlation correction. In a systematic study, Feller [9] reported estimates of the complete basis set (CBS) limit for the mean dipole polarizability ($\bar{\alpha}$) and first mean dipole hyperpolarizability ($\bar{\beta}$) quite close to the previous values [1], but his estimates of the full configuration

* E-mail: marou@upatras.gr

interaction (FCI) limit of the corresponding electron correlation corrections are rather small in magnitude compared to those obtained from fourth-order Møller–Plesset perturbation theory [1].

In this Letter we present estimates of the Hartree–Fock limit of the first and second dipole hyperpolarizability of the water molecule. Thence we proceed to obtain evidence for the true size of electron correlation effects for these properties. The present interest in the nonlinear optics of small molecules [11] has made the convergence of theory and experiment a challenge for quantum chemistry. We include in this study the electric multipole moments and the dipole polarizability in order to ensure the overall quality of the LCAO–SCF–MO wavefunctions used in the calculations. The rapidly expanding range of applications of the electric moments and polarizability in fields related to the theory of intermolecular interactions [12,13] justifies the need for accurate values. It is worth mentioning that refined approaches to simulation studies of phases involving the water molecule include the effects of the electric hyperpolarizability [14,15].

Atomic units are used throughout this Letter. The relevant conversion factors to SI units are: energy, 1 $E_h = 4.3597482 \times 10^{-18}$ J; length, 1 $a_0 = 0.529177249 \times 10^{-10}$ m; μ , 1 $ea_0 = 8.478358 \times 10^{-30}$ C m; Θ , 1 $ea_0^2 = 4.486554 \times 10^{-40}$ C m²; Ω , 1 $ea_0^3 = 2.374182 \times 10^{-50}$ C m³; Φ , 1 $ea_0^4 = 1.256363 \times 10^{-60}$ C m⁴; α , 1 $e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41}$ C² m² J⁻¹; β , 1 $e^3 a_0^3 E_h^{-2} = 3.206361 \times 10^{-53}$ C³ m³ J⁻²; and γ , 1 $e^4 a_0^4 E_h^{-3} = 6.235378 \times 10^{-65}$ C⁴ m⁴ J⁻³.

2. Theory

The interaction of a neutral molecule with a weak, static electric field results in a distortion of the electron density. The energy of the perturbed system is adequately described by the expansion [16]

$$\begin{aligned}
 E^p &= E^p(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, \dots) \\
 &= E^0 - \mu_\alpha F_\alpha - (1/3)\Theta_{\alpha\beta} F_{\alpha\beta} - (1/15)\Omega_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - (1/105)\Phi_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} + \dots \\
 &\quad - (1/2)\alpha_{\alpha\beta} F_\alpha F_\beta - (1/3)A_{\alpha,\beta\gamma} F_\alpha F_{\beta\gamma} - (1/6)C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} \\
 &\quad - (1/15)E_{\alpha,\beta\gamma\delta} F_\alpha F_{\beta\gamma\delta} + \dots \\
 &\quad - (1/6)\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/6)B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} + \dots \\
 &\quad - (1/24)\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots
 \end{aligned} \tag{1}$$

where F_α , $F_{\alpha\beta}$, etc., are the field, field gradient, etc., respectively, at the origin. E^0 and μ_α , $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ are the energy and the dipole, quadrupole, octopole and hexadecapole moment, respectively, of the free molecule. The second-, third- and fourth-order properties are the dipole and quadrupole polarizabilities and hyperpolarizabilities $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$, $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. The subscripts denote Cartesian components and a repeated subscript implies summation over x , y and z . The number of independent components needed to specify the electric multipole moment and polarizability tensors of a molecule of C_{2v} symmetry, as H_2O , is well known [16]. The present choice of particular components reflects a widely accepted choice for all properties.

Our approach to the calculation of the electric properties is essentially a finite-field method. A detailed presentation of our method for the calculation of the dipole properties and the quadrupole moment may be found elsewhere [17,18]. Values of the quadrupole, octopole and hexadecapole moment were also obtained from the MP2 density [19].

In addition to the Cartesian components we also compute the mean and the anisotropy of the dipole polarizability and the mean first and second dipole hyperpolarizability defined as

$$\begin{aligned}\bar{\alpha} &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \\ \Delta\alpha &= (1/2)^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \\ \bar{\beta} &= (3/5)(\beta_{zzx} + \beta_{zyy} + \beta_{zzz}) \\ \bar{\gamma} &= (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})\end{aligned}\quad (2)$$

Detailed discussions of the Møller–Plesset (MP) and coupled cluster (CC) theory may be found in standard references or comprehensive reviews [20–22]. We give here the definitions of the various orders of the MP n approximation to the molecular energy, useful in the analysis of the correlated values of the molecular properties:

$$\begin{aligned}\text{MP2} &= \text{SCF} + \text{D2} \\ \text{MP3} &= \text{MP2} + \text{D3} \\ \text{DQ-MP4} &= \text{MP3} + \text{D4} + \text{QR4} = \text{MP3} + \text{DQ4} \\ \text{SDQ-MP4} &= \text{DQ-MP4} + \text{S4} \\ \text{MP4} &= \text{SDQ-MP4} + \text{T4} = \text{SCF} + \text{D2} + \text{D3} + \text{S4} + \text{D4} + \text{T4} + \text{Q4} + \text{R4}\end{aligned}\quad (3)$$

For the CC methods

$$\begin{aligned}\text{CCSD} &= \text{SCF} + \Delta\text{CCSD} \\ \text{CCSD(T)} &= \text{CCSD} + \text{T}\end{aligned}\quad (4)$$

Similar expansions are adopted for the molecular properties and the mean values defined in Eq. (4), with the exception of the anisotropy $\Delta\alpha$. Its values at a given level of theory are obtained from the pertinent α_{xx} , α_{yy} and α_{zz} quantities.

3. Basis set construction and computational strategy

We aim at obtaining hyperpolarizability values at the highest possible level of theory with a basis set of quasi-Hartree–Fock quality. To avoid systematic errors we do not use basis sets built upon the same substrates as those employed in our previous study [1]. Highly flexible, well-optimized basis sets built upon strong substrates of recent construction are used in this work. The first substrate is a set of (12s 7p / 6s) primitive gaussian-type functions (GTF) contracted to [7s 4p / 4p] [23]. The second is a larger, uncontracted set of (14s 9p / 9s) GTF [24,25]. We use a technique applied successfully to the construction of basis sets for electric polarizability calculations [26]. Diffuse s- and p-GTF (on oxygen) and s-GTF (on hydrogen) are added to the substrate. Next, tight p-GTF (on H) and d-GTF (on O) are added with exponents chosen to minimize the energy of the free molecule followed by diffuse p-GTF (on H) and d-GTF (on O) with exponents chosen to maximize the mean dipole polarizability $\bar{\alpha}$. Additional p-GTF (on H) and d-GTF (on O) are added even-temperedly. The construction is completed with addition of f-GTF on oxygen and d- and f-GTF on hydrogen. Thus, from [7s 4p / 4s] we obtained the basis sets [9s 6p 6d 3f / 6s 4p 2d 1f], hereafter KT1, consisting of 148 CGTF and [9s 6p 6d 4f / 6s 5p 3d 2f], hereafter KT2, or 185 CGTF. A much larger uncontracted basis set was obtained from

(14s 9p / 9s), (18s 13p 8d 5f / 12s 7p 3d 2f), hereafter PA, or 256 GTF. 5d/7f GTF were used in all cases. The composition of the three basis sets has as follows (exponents in a_0^{-2}):

$$\begin{aligned}
 \text{KT1} &= [7s4p/4s] + (\text{O: } s = 0.07733, 0.02874, p = 0.05302, \\
 &\quad 0.01898, d = 2.96093, 1.10388, 0.41154, 0.15343, 0.05720, \\
 &\quad 0.02133, f = 1.10388, 0.15343, 0.05720/\text{H: } s = 0.031302, \\
 &\quad 0.010891, p = 0.77904, 0.14890, 0.06510, 0.02846, \\
 &\quad d = 0.77904, 0.14890, f = 0.14890) \\
 \text{KT2} &= \text{KT1} + (\text{O: } f = 0.41154/\text{H: } p = 1.78194, d = 0.06510, \\
 &\quad f = 0.77904) \\
 \text{PA} &= (14s9p/9s) + (\text{O: } s = 0.072459, 0.028849, 0.011486, \\
 &\quad 0.004573, p = 0.046088, 0.018642, 0.00754, 0.00305, \\
 &\quad d = 1.8040, 1.0930, 0.6622, 0.4012, 0.2431, 0.1473, \\
 &\quad 0.0541, 0.0199, f = 1.0930, 0.4012, 0.2431, 0.1473, \\
 &\quad 0.0541/\text{H: } s = 0.0280548, 0.0117535, 0.0049241, \\
 &\quad p = 1.8303, 1.1948, 0.7799, 0.3323, 0.1416, 0.0603, \\
 &\quad 0.0257, d = 0.7799, 0.1416, 0.0603, f = 0.7799, 0.1416)
 \end{aligned}$$

The dipole properties were calculated from the energy of the molecule perturbed by homogeneous electric fields of strength ± 0.005 , ± 0.01 and ± 0.02 $e^{-1}a_0^{-1}E_h$. For the quadrupole moment we used arrays of distant charges $-32Q, Q, Q, -32Q$ placed on each axis at $-2R, -R, R, 2R$ and producing a weak quadrupolar field with $|Q/R^3| = 0.000001$ $e^{-1}a_0^{-2}E_h$.

Table 1

Self-consistent field values for the dipole moment, dipole polarizability, first and second dipole hyperpolarizability of H_2O

P	KT1 148 CGTF	KT2 185 CGTF	PA ^a 256 GTF	W5 ^b 136 CGTF	W4 ^b 138 CGTF
μ_z	0.7790	0.7795	0.7797	0.7789	0.7787
α_{xx}	9.1799	9.1818	9.1794	9.176	9.178
α_{yy}	7.8965	7.9015	7.8996	7.896	7.888
α_{zz}	8.5207	8.5244	8.5223	8.522	8.522
$\bar{\alpha}$	8.5323	8.5359	8.5338	8.531	8.529
$\Delta\alpha$	1.1116	1.1089	1.1085	1.109	1.117
β_{zxx}	-9.35	-9.38	-9.40	-9.35	-9.39
β_{zyy}	-1.42	-1.39	-1.35	-1.31	-1.35
β_{zzz}	-7.69	-7.72	-7.71	-7.44	-7.56
$\bar{\beta}$	-11.07	-11.10	-11.07	-10.86	-10.98
γ_{xxxx}	568	566	569	564	567
γ_{yyyy}	1428	1436	1422	1414	1420
γ_{zzzz}	902	903	907	906	897
γ_{xxyy}	335	336	338	335	337
γ_{yyzz}	388	388	389	384	386
γ_{zzxx}	287	287	287	286	285
$\bar{\gamma}$	984	986	985	979	980

^aSCF $E^0 = -76.0669005546$ E_h .

^bRef. [1].

Table 2

Electron correlation corrections^a to the SCF values of μ_α , $\Theta_{\alpha\beta}$, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ calculated with KT1 $\equiv [9s\ 6p\ 6d\ 3f / 6s\ 4p\ 2d\ 1f]$, 148 CGTF (the quadrupole moment^b is relative to the centre of mass)

P	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4	CCSD	CCSD(T)
μ_z	0.7790	0.7286	0.7386	0.7366	0.7298	0.7183	0.7317	0.7231
Θ_{xx}	1.8968	1.9466	1.9019	1.9050	1.9084	1.9177	1.9049	1.9084
Θ_{yy}	−1.7926	−1.8362	−1.7979	−1.7993	−1.8000	−1.8062	−1.7986	−1.8006
Θ_{zz}	−0.1041	−0.1104	−0.1040	−0.1057	−0.1084	−0.1116	−0.1063	−0.1077
α_{xx}	9.1799	9.9830	9.6381	9.6806	9.8174	10.0461	9.7714	9.9297
α_{yy}	7.8965	9.5399	8.8047	8.9025	9.1330	9.5262	9.0678	9.3359
α_{zz}	8.5207	9.7298	9.1839	9.2608	9.4467	9.7661	9.3734	9.5877
$\bar{\alpha}$	8.5323	9.7509	9.2089	9.2813	9.4657	9.7795	9.4042	9.6178
$\Delta\alpha$	1.1116	0.3850	0.7227	0.6745	0.5934	0.4506	0.6111	0.5162
β_{zxx}	−9.35	−9.11	−8.95	−9.03	−9.64	−10.06	−9.48	−9.80
β_{zyy}	−1.42	−5.65	−3.12	−3.60	−4.95	−6.55	−4.58	−5.61
β_{zzz}	−7.69	−14.08	−9.91	−10.80	−13.17	−16.03	−12.04	−13.77
$\bar{\beta}$	−11.07	−17.30	−13.18	−14.06	−16.66	−19.58	−15.66	−17.51
γ_{xxxx}	568	847	681	709	796	910	762	834
γ_{yyyy}	1428	2681	1988	2113	2449	2856	2379	2656
γ_{zzzz}	902	1513	1151	1224	1403	1634	1329	1476
γ_{xxzz}	335	630	469	496	576	674	563	630
γ_{yyzz}	388	714	528	563	655	767	635	710
γ_{zxxx}	287	440	352	369	417	475	402	440
$\bar{\gamma}$	984	1722	1304	1380	1589	1847	1534	1705

^aThe innermost occupied orbital was kept frozen while excitations were not allowed to the two highest unoccupied ones.

^bOnly two of the listed values are independent as $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$.

All calculations pertain to the experimental equilibrium geometry, defined by $R_{OH} = 0.9572\text{ \AA}$ and a HOH angle of 104.52° [27]. The molecule is on the xz plane, with z as the C_2 axis, the centre of mass at the origin and the oxygen nucleus on the negative z axis.

The Gaussian 92 and Gaussian 94 programmes were used in this work [28,29].

4. Results and discussion

Table 1 lists the SCF values for the dipole properties obtained with the KT1, KT2 and PA basis sets. We also give two sets of values from our previous study [1]. In Table 2 we display an analysis of the electron correlation effects for these properties calculated with KT1. Table 3 contains additional results for the electric multipole moments at the SCF and MP2 levels of theory. Last, experimental results and theoretical predictions are compared in Table 4.

The convergence of the present SCF values to the Hartree–Fock limit is, we hope, fairly obvious from the contents of Tables 1 and 3. Basis sets KT2 and PA are quite different, with regard to the original substrate and the construction. The agreement of the SCF/KT2 and SCF/PA results extends from the first- to the third- and fourth-order properties. The latter are notoriously sensitive to basis set quality. The agreement for the components of $\gamma_{\alpha\beta\gamma\delta}$ is significantly better than 1% in all cases. The mean value of $\gamma_{\alpha\beta\gamma\delta}$ is 986 (KT2) and 985

Table 3

Electric multipole moments of H₂O at the SCF and MP2 level of theory (the quadrupole, octopole^a and hexadecapole moments are relative to the centre of mass)

P	SCF/KT1	MP2/KT1	SCF/KT2	MP2/KT2	SCF/PA
μ_z	0.7790	0.7286	0.7795	0.7284	0.7797
Θ_{xx}	1.8968	1.9466	1.9000	1.9502	1.8998
Θ_{yy}	−1.7927	−1.8362	−1.7965	−1.8405	−1.7957
Θ_{zz}	−0.1041	−0.1104	−0.1035	−0.1097	−0.1040
Ω_{xxz}	3.2778	3.2407	3.2879	3.2544	3.2823
Ω_{yyz}	−1.3488	−1.3514	−1.3554	−1.3585	−1.3390
Ω_{zzz}	−1.9290	−1.8894	−1.9325	−1.8959	−1.9433
Φ_{xxxx}	−1.21	−0.93	−1.21	−0.93	−1.23
Φ_{yyyy}	4.06	3.99	4.06	3.99	4.13
Φ_{zzzz}	−3.79	−3.55	−3.81	−3.59	−3.81

^a Only two of the listed values are independent as $\Omega_{xxz} + \Omega_{yyz} + \Omega_{zzz} = 0$.

(PA) $e^4 a_0^4 E_h^{-3}$, two practically identical results. It is worth noticing the close agreement between the SCF/KT1 and SCF/PA values. Observe the closeness of the $\alpha_{\alpha\beta}$ ($e^2 a_0^2 E_h^{-1}$), $\beta_{\alpha\beta\gamma}$ ($e^3 a_0^3 E_h^{-2}$) and $\gamma_{\alpha\beta\gamma\delta}$ ($e^4 a_0^4 E_h^{-3}$) results: $\bar{\alpha} = 8.5323$, $\bar{\beta} = -11.07$ and $\bar{\gamma} = 984$ for KT1, to be compared to the respective 8.5338, -11.07 and 985 for PA. Thus, KT1 is clearly of near-Hartree–Fock quality.

Electron correlation changes significantly the SCF/KT1 values, with the notable exception of the quadrupole moment where the effect is small for all components. A striking fact is the size of the $D2$ correction. The MP2 and MP3 values are very dissimilar for all properties. In some cases the MP2 values are remarkably close to the CCSD(T) ones. Electron correlation halves the $\Delta\alpha$ value but increases, in absolute terms, the mean SCF $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$ by 12.8%, 58.2% and 42.3%, respectively. The most important case is the components of the $\beta_{\alpha\beta\gamma}$ tensor. The relative magnitude of the SCF values is greatly modified from MP2 through MP4. Last, we observe that the MP2/KT1 and MP2/KT2 octopole and hexadecapole moment values are only a few percent different from the respective SCF ones. This is, quite probably, an indication that our MP2 values are accurate enough to represent reliable predictions for the higher moments.

This most important part of this Letter encompasses the arguments supporting the conclusive character of our findings. In Table 4 we display the SCF/PA results, expected to be of near-Hartree–Fock quality for all properties. Our best values, SCF + ECC, are obtained by adding to the SCF/PA the CCSD(T)/KT1 electron correlation correction (ECC) with the exception of the octopole and hexadecapole moment where the listed values are SCF/PA plus the D2/KT2 correction. The $\Delta\alpha$ value in this column is just the CCSD(T)/KT1 one from Table 2. In previous work [1] we relied on MP4 calculations to advance the following estimates of the ECC: -0.055 ± 0.005 for μ_z (ea_0), 1.11 ± 0.14 for $\bar{\alpha}$ ($e^2 a_0^2 E_h^{-1}$), -7.1 ± 1.3 for $\bar{\beta}$ ($e^3 a_0^3 E_h^{-2}$) and 749 ± 113 $e^4 a_0^4 E_h^{-3}$ for $\bar{\gamma}$ ($e^4 a_0^4 E_h^{-3}$). The CCSD(T)/KT1 calculations yield ECC values of -0.0559 , 1.09 , -6.44 and 721 , respectively. Thus, the present values corroborate the previous estimates. Our SCF + ECC μ_α and $\Theta_{\alpha\beta}$ values agree well with the MRSDCI (multireference single and double excitation configuration interaction) results of Bündgen et al. [30]. Feller [9] has obtained estimates for several molecular properties of the water molecule at the CBS–FCI (complete basis set full configuration interaction) limit. Our μ_α , $\Theta_{\alpha\beta}$ and $\Omega_{\alpha\beta\gamma}$ values are quite close to Feller's values. The agreement does not extend to the dipole polarizability and hyperpolarizability. Our SCF/PA values for $\bar{\alpha}$ ($e^2 a_0^2 E_h^{-1}$) and $\bar{\beta}$ ($e^3 a_0^3 E_h^{-2}$) are in almost perfect agreement with his CBS estimates but the respective ECC, 1.09 and -6.44 , are significantly larger in magnitude than his CBS–FCI of 0.75 and -3.9 . Our SCF + ECC values for the dipole moment, polarizability and hyperpolarizability are in good agreement with the CCSD(T) ones of Sekino and Bartlett [6]. With the notable exception of μ_z and $\Delta\alpha$, their values are almost systematically larger in magnitude than ours. For $\gamma_{\alpha\beta\gamma\delta}$ the difference goes

up to 10% for some components but their $\bar{\gamma} = 1800 \text{ e}^4 a_0^4 E_h^{-3}$ is only 5.5% above our SCF + ECC value of 1706 $\text{e}^4 a_0^4 E_h^{-3}$. We note that our results for $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are also in reasonable agreement with those reported in an interesting study by Luo et al. [8]. Spelsberg and Meyer [10] reported $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ values calculated with the

Table 4

Comparison of theoretical predictions and experimental data for the electric properties of H_2O

Property	Near HF > ^a	SCF + ECC ^b	Previous theoretical	Experiment
μ_z	0.7797	0.7238	0.723 ^c , 0.730 ^d , 0.7196 ^e	0.7268 ^f , 0.7306 ^g
Θ_{xx}	1.8998	1.912	1.900 ^c , 1.909 ^d	1.96 ± 0.02 ^h
Θ_{yy}	−1.7957	−1.804	−1.805 ^c , −1.801 ^d	−1.86 ± 0.02 ^h
Θ_{zz}	−0.1040	−0.108	−0.095 ^c , −0.108 ^d	−0.10 ± 0.02 ^h
Ω_{xxz}	3.2823	3.25	3.206 ^d	
Ω_{yyz}	−1.3390	−1.34	−1.332 ^d	
Ω_{zzz}	−1.9433	−1.91	−1.874 ^d	
Φ_{xxxx}	−1.23	−0.95		
Φ_{yyyy}	4.13	4.06		
Φ_{zzzz}	−3.81	−3.59		
α_{xx}	9.1794	9.93	9.77 ⁱ , 10.02 ^c , 10.29 ⁱ	10.31 ± 0.08 ^k
α_{yy}	7.8996	9.34	9.28 ⁱ , 9.64 ^c , 9.30 ^j	9.55 ± 0.08 ^k
α_{zz}	8.5223	9.59	9.44 ⁱ , 9.73 ^c , 9.72 ^j	9.91 ± 0.02 ^k
$\bar{\alpha}$	8.5338	9.62	9.3 ^d , 9.50 ⁱ , 9.79 ^c , 9.72 ^j	9.83 ± 0.02 ^l
$\Delta\alpha$	1.1085	0.52	0.43 ⁱ , 0.34 ^c , 0.86 ^j	0.67 ± 0.05 ^k
β_{zxx}	−9.40	−9.8	−8.93 ⁱ , −10.2 ^c	
β_{zyy}	−1.35	−5.5	−5.11 ⁱ , −6.2 ^c	
β_{zzz}	−7.71	−13.8	−12.10 ⁱ , −13.7 ^c	
$\bar{\beta}$	−11.07	−17.5	−15.0 ^d , −15.68 ⁱ , −18.0 ^c	−19.2 ± 0.9 ^m , −22.0 ± 0.9 ⁿ
γ_{xxxx}	569	836	820 ^c	
γ_{yyyy}	1422	2650	2900 ^c	
γ_{zzzz}	907	1481	1500 ^c	
γ_{xxyy}	338	633	680 ^c	
γ_{yyzz}	389	711	770 ^c	
γ_{zzxx}	287	439	440 ^c	
$\bar{\gamma}$	985	1706	1800 ^c	1800 ± 150 ^m , 2310 ± 120 ⁿ

^aPresent investigation, PA results.

^bPresent investigation. SCF/PA + electron correlation correction (ECC) from CCSD(T)/KT1 for all properties with the exception of Ω and Φ where SCF/PA + D2/KT2 values are listed. For $\Delta\alpha$ the CCSD(T)/KT1 value is given.

^cBündgen et al. [30].

^dFeller [9].

^eSekino and Bartlett (basis 3) [6].

^fClough et al. [31].

^gShostak et al. [2].

^hVerhoeven and Dymanus [32].

ⁱCAS1/P3 results, Luo et al. [8].

^jSpelsberg and Meyer [10].

^kDynamic values (514.5 nm) by Murphy [33].

^lStatic value referenced by Russell and Spackman [34].

^mGas-phase EFISH at 1064 nm by Kaatz et al. [3].

ⁿGas-phase EFISH at 694.3 nm by Ward and Miller, rescaled value, see Shelton and Rice [11].

SE–MRCI (single-excitation multireference CI) method at a molecular geometry obtained by averaging over the zero-point vibration. Although our results pertain to the equilibrium geometry, the similarity of their findings to ours is fairly obvious and will be borne out below. Other efforts, at levels of theory comparable to the SCF one employed in this Letter, include the dynamic $\beta_{\alpha\beta\gamma}$ values reported by Parkinson and Oddershede [5] and the density functional theory results for $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ reported by Guan et al. [7]. Older results for the dipole properties are discussed in our previous paper [1].

The equilibrium dipole moment reported in this Letter is within 1% of the respective experimental values of Clough et al. [31] and Shostak et al. [2]. To compare our values for $\Theta_{\alpha\beta}$ (ea_0^2) to the experimental data of Verhoven and Dymanus [32] we add to SCF + ECC results the zero-point vibrational correction (ZPVC) computed at the MP2 level by Russell and Spackman [34]. We obtain SCF + ECC + ZPVC values of $\Theta_{xx} = 1.956$, $\Theta_{yy} = -1.855$ and $\Theta_{zz} = -0.101$, in excellent agreement with the experimental data listed in Table 4. For the dipole polarizability and hyperpolarizability we propose the following values as estimates of the respective static limits, $\bar{\alpha} = 9.62 \pm 0.03$ and $\Delta\alpha = 0.52 \pm 0.02$ $e^2a_0^2E_h^{-1}$, $\bar{\beta} = -17.5 \pm 0.3$ $e^3a_0^3E_h^{-2}$ and $\bar{\gamma} = (171 \pm 6) \times 10^1$ $e^4a_0^4E_h^{-3}$. The MP2 ZPVC [32] for $\bar{\alpha}$ is estimated at 0.29 $e^2a_0^2E_h^{-1}$. Added to our value gives a SCF + ECC + ZPVC $\bar{\alpha} = 9.91 \pm 0.03$ $e^2a_0^2E_h^{-1}$, 0.8% higher than the experimental value of 9.83 ± 0.02 (see Russell and Spackman [34]). The CCSD(T)/K1 + ZPVC $\Delta\alpha = 0.75$ $e^2a_0^2E_h^{-1}$ is higher than the dynamic value (514.5 nm) reported by Murphy [33]. It should be emphasized that the available theoretical values point to a ZPVC of $\sim 3\%$ for $\bar{\alpha}$ [34] but the calculation of a very accurate estimate should be quite difficult. We judge important to compare at this point our findings to the SE–MRCI [10] values $\alpha_{\alpha\beta}$ ($e^2a_0^2E_h^{-1}$). Spelsberg and Meyer [10] obtained $\bar{\alpha} = 9.77$ and $\Delta\alpha = 0.86$, close to our SCF + ECC + ZPVC values. Their respective electron correlation corrections are 1.04 ($\bar{\alpha}$) and -0.47 ($\Delta\alpha$), very close to our equilibrium ECC values of 1.09 and -0.59 . We rely on the study by Luo et al. [8] for a meaningful comparison of our value for $\bar{\beta}$ to the experimental data. The CASSCF (complete active space SCF) results of these authors (CAS1/P3 values) give a ZPVC of -1.38 $e^3a_0^3E_h^{-2}$ for the static limit of $\bar{\beta}$. Adding this quantity to our SCF + ECC gives a static SCF + ECC + ZPVC value of -18.9 ± 0.3 $e^3a_0^3E_h^{-2}$, in excellent agreement with the -19.4 $e^3a_0^3E_h^{-2}$ SE–MRCI value [10] and quite plausibly close to the -19.2 ± 0.9 $e^3a_0^3E_h^{-2}$ extracted from EFISH measurements at 1064 nm by Kaatz et al. [3]. At 694.3 nm Luo et al. [8] obtained -20.85 $e^3a_0^3E_h^{-2}$, in very reasonable agreement with the experimental value of -22.0 ± 0.9 $e^3a_0^3E_h^{-2}$ reported by Ward and Miller (rescaled value, see Shelton and Rice [11]). There is no available ZPVC value for $\bar{\gamma}$. One might hazard an inspired guess for its magnitude: $10 \pm 5\%$ of the static SCF + ECC value of 1706 $e^4a_0^4E_h^{-3}$. Any value in this range would bring the theoretical prediction rather close to the EFISH value of 1800 ± 150 $e^4a_0^4E_h^{-3}$ at 1064 nm [3]. The EFISH value of $\bar{\gamma}(\text{D}_2\text{O})$ at 1064 nm is 1660 ± 220 $e^4a_0^4E_h^{-3}$ [3], $\sim 8\%$ below the $\bar{\gamma}(\text{H}_2\text{O})$ result. The older experimental value by Ward and Miller is 2310 ± 120 $e^4a_0^4E_h^{-3}$ at 694.3 nm (see Shelton and Rice [11]). Sekino and Bartlett [6] estimate the dispersion of $\bar{\gamma}$ at 400 $e^4a_0^4E_h^{-3}$ for 694.3 nm. Again, if this quantity is added to our estimate of $(171 \pm 6) \times 10^1$ $e^4a_0^4E_h^{-3}$, agreement between theory and experiment springs up.

5. Conclusions

We have obtained values close to the Hartree–Fock limit for the first and second dipole hyperpolarizability of H_2O . Electron correlation corrections were calculated at the CCSD(T) level of theory with a basis set of near-Hartree–Fock quality. The present values of the EEC to μ_z , $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$ corroborate the validity of the previous estimates obtained from fourth-order Møller–Plesset calculations [1]. The ECC $\bar{\alpha}$ and $\bar{\beta}$ values are larger in magnitude than the CBS–FCI estimates reported by Feller [9].

We propose $\bar{\beta} = -17.5 \pm 0.3$ $e^3a_0^3E_h^{-2}$ and $\bar{\gamma} = (171 \pm 6) \times 10^1$ $e^4a_0^4E_h^{-3}$ for the static limit of these properties at the experimental equilibrium geometry. Agreement between these values and the new EFISH measurements is easily deduced.

Other fruits of this endeavour are the very accurate values of the components of the quadrupole moment and the dipole polarizability tensor: $\Theta_{xx} = 1.912$, $\Theta_{yy} = -1.804$, $\Theta_{zz} = -0.108$ for $\Theta_{\alpha\beta}$ (ea_0^2) and $\alpha_{xx} = 9.93$,

$\alpha_{yy} = 9.34$, $\alpha_{zz} = 9.59$ for $\alpha_{\alpha\beta}$ ($e^2 a_0^2 E_h^{-1}$). Last, we have obtained reliable values for the octopole and hexadecapole moment.

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References

- [1] G. Maroulis, J. Chem. Phys. 94 (1991) 1182.
- [2] S.L. Shostak, W.L. Ebenstein, J.S. Muentner, J. Chem. Phys. 94 (1991) 5875.
- [3] P. Kaatz, E.A. Donley, D.P. Shelton, J. Chem. Phys. 108 (1998) 849.
- [4] J.E. Bloor, J. Mol. Struct. (Theochem) 234 (1991) 173.
- [5] W.A. Parkinson, J. Oddershede, J. Chem. Phys. 94 (1991) 7251.
- [6] H. Sekino, R.J. Bartlett, J. Chem. Phys. 98 (1993) 3022.
- [7] J. Guan, P. Duffy, J.T. Carter, D.P. Chong, K.C. Casida, M.E. Casida, M. Wrinn, J. Chem. Phys. 98 (1993) 4753.
- [8] Y. Luo, H. Ågren, O. Vahtras, P. Jørgensen, V. Spirko, H. Hettema, J. Chem. Phys. 98 (1993) 7159.
- [9] D. Feller, J. Chem. Phys. 98 (1993) 7059.
- [10] D. Spelsberg, W. Meyer, J. Chem. Phys. 108 (1998) 1532.
- [11] D.P. Shelton, J.E. Rice, Chem. Rev. 94 (1994) 3.
- [12] C.G. Gray, K.E. Gubbins, Theory of Molecular Fluids, vol. 1, Clarendon, Oxford, 1984.
- [13] A.J. Stone, The Theory of Intermolecular Forces, Clarendon, Oxford, 1996.
- [14] B. Yang, D.E. Sullivan, B. Tjpto-Margo, C.G. Gray, J. Phys. F 3 (1991) 109.
- [15] G. Ruocco, M. Sampoli, Mol. Phys. 82 (1994) 875.
- [16] A.D. Buckingham, Adv. Chem. Phys. 12 (1967) 107.
- [17] G. Maroulis, J. Chem. Phys. 108 (1998) 5432.
- [18] G. Maroulis, Chem. Phys. Lett. 177 (1991) 352.
- [19] K.B. Wiberg, C.M. Hadad, T.J. LePage, C.M. Breneman, M.J. Frisch, J. Am. Chem. Soc. 96 (1992) 671.
- [20] A. Szabo, N.S. Ostlund, Modern Quantum Chemistry, Macmillan, New York, 1982.
- [21] M. Urban, I. Cernusak, V. Kellö, J. Noga, Methods, Methods Comput. Chem. 1 (1987) 117.
- [22] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1987) 479.
- [23] A.J. Thakkar, T. Koga, M. Saito, R.E. Hoffmeyer, Int. J. Quant. Chem. S27 (1993) 343.
- [24] H. Partridge, Near Hartree–Fock quality gaussian type orbital basis sets for the second-row atoms, NASA (Natl. Aeron. Space Adm.) Tech. Mem. 89449, May 1987.
- [25] H. Partridge, Near Hartree–Fock quality gaussian type orbital basis sets for the first- and third-row atoms, NASA (Natl. Aeron. Space Adm.) Tech. Mem. 101044, Jan. 1989.
- [26] G. Maroulis, J. Phys. Chem. 100 (1996) 13466.
- [27] W.S. Benedict, N. Gailar, E.K. Plyler, J. Chem. Phys. 24 (1956) 1139.
- [28] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, J.A. Pople, GAUSSIAN 92, Revision C, Gaussian, Pittsburgh, PA, 1992.
- [29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, and J.A. Pople, GAUSSIAN 94, Revision E.1, Gaussian, Pittsburgh, PA, 1995.
- [30] P. Bündgen, F. Grein, A.J. Thakkar, J. Mol. Struct. (Theochem) 334 (1995) 7.
- [31] S.A. Clough, Y. Beers, G.P. Klein, S.L. Rothman, J. Chem. Phys. 59 (1973) 2254.
- [32] J. Verhoeven, A. Dymanus, J. Chem. Phys. 52 (1985) 3222.
- [33] W.F. Murphy, J. Chem. Phys. 67 (1977) 5877.
- [34] A.J. Russell, M.A. Spackman, Mol. Phys. 84 (1995) 1239.