***Ab initio* dipole polarizability surfaces of water molecule: Static and dynamic at 514.5 nm**

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Coupled cluster calculations with a carefully designed basis set have been performed to obtain both static, α , and dynamic at 514.5 nm, $\alpha(514.5 \text{ nm})$, dipole polarizability surfaces of water. We employed a medium size basis set ($13s10p6d3f/9s6p2d1f$)[$9s7p6d3f/6s5p2d1f$] consisting of 157 contracted Gaussian-type functions that yields values near the Hartree–Fock limit for α [G. Maroulis, J. Chem. Phys. **94**, 1182 (1991)]. The α and $\alpha(514.5 \text{ nm})$ surfaces were able to reproduce all the experimentally available information about the dipole polarizability of water, especially the Raman spectra of gaseous H_2O , D_2O , and HDO . Vibrational averages for the dipole polarizability of water molecule are also reported. © 2005 American Institute of Physics.
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I. INTRODUCTION

The current interest in the dipole polarizability of water is reflected in several experimental and theoretical studies reported in recent years. Important areas of application include spectroscopic investigations,^{1,2} simulation studies,^{3,4} treatments of the intermolecular interactions,^{5,6} and investigations on the weakly bound van der Waals complexes of this important molecule.^{7,8} Water dipole polarizability derivatives with respect to the internal motions of the nuclei find their main application in the calculation of the rotation-vibration Raman spectra and to account for nonlinear electrotropical effects.⁹ Moreover, they are necessary in the theoretical study about the intramolecular dependence of the potential surface of the dimer $(\text{H}_2\text{O})_2$, and for the analysis of its infrared¹⁰ and Raman spectrum in the region of the fundamental vibrations of the monomers.

Various aspects about the theoretical determination of molecular electric polarizabilities have been examined in some depth in comprehensive reviews.¹¹ The accuracy of *ab initio* calculations of dipole polarizabilities critically depends on elements of several categories, to mention: basis sets, electron correlation, frequency dependencies, and vibrational corrections. Basis sets evidently need the flexibility to represent correctly any polarization of the electronic cloud and therefore they should describe the tail regions of electron distribution properly. Electron correlation has been found to be essential for many molecules since it could affect the self-consistent-field values beyond 10%. The experimental data like the rotation-vibration Raman spectra and the refractive index measurements always refer to frequency dependent processes and they are related to dynamic dipole polarizabilities. The extrapolation to zero frequency may be a satisfactory alternative, but it often introduces problems for the comparison between theory and experiment and it is therefore preferable to carry out calculations of dynamic di-

pole polarizabilities. Finally, the importance of vibrational corrections for molecular electric properties like the dipole polarizability has become well known and accepted since Bishop first drew particular attention to it,¹² and several articles have devoted to this topic.¹³

We report here the *ab initio* static, α , and dynamic at 514.5 nm, $\alpha(514.5 \text{ nm})$, dipole polarizability surfaces of water for the first time. The quality of the $\alpha(514.5 \text{ nm})$ surface presented here has been checked through an accurate simulation of the rotation-vibration Raman spectra of gaseous H_2O , D_2O , and HDO .^{14–16} The paper is organized as follows: in the following section we discuss the basis set, the internal nuclear coordinates, the axis system, and two different methods for obtaining *ab initio* dipole polarizabilities. In Sec. III, we analyze the quality of the basis set and the electron correlation effects, present the dipole polarizability surfaces, and discuss comparison with experimental data. In Sec. IV, vibrational averages of the dipole polarizability for H_2O , D_2O , and HDO are reported. Finally, in Sec. V, we give some conclusions.

Unless otherwise indicated, atomic units for dipole polarizability, length, and energy are used throughout this paper. The relevant conversion factors from atomic to SI units are $a_0 = 0.529\,177\,249 \times 10^{-10} \text{ m}$ for length, $E_h = 4.359\,748\,2 \times 10^{-18} \text{ J}$ for energy, and $e^2 a_0^2 E_h^{-1} = 1.648\,778 \times 10^{-41} \text{ CV}^{-1} \text{ m}^2$ for the dipole polarizability.

II. THEORY AND COMPUTATIONAL DETAILS

In this work, we aim at obtaining dipole polarizability values at high levels of theory using an optimized basis set consisting of Gaussian-type functions (GTFs) that yields electric properties of near-Hartree–Fock quality. Thus, our post-Hartree–Fock calculations use as starting point high quality zeroth-order wave functions. The choice of suitable basis sets has been recognized as a key factor in molecular property calculations,¹⁷ but choice is always based on empirical arguments for their use in theoretical predictions of most types of properties. With this idea on mind, our *ab*

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initio calculations have been performed in order to get accurate simulations of the rotation-vibration Raman spectrum of water with an acceptable computational expense. The W_6 basis set ($13s10p6d3f/9s6p2d1f$) [$9s7p6d3f/6s5p2d1f$] that we have used to calculate the static and dynamic at 514.5 nm dipole polarizability surfaces was built up adding a f -GTF on hydrogen atoms with exponent $0.1a_0^{-2}$ and a f -GTF on oxygen atom with exponent $0.2a_0^{-2}$ to the W_5 basis set presented by Maroulis.¹⁸ Six larger basis sets KT3, KT4, PA, PA1, PA2, and PA3 were used in order to study electron correlation and basis set truncation effects. PA is a large ($18s13p8d5f/12s7p3d2f$) basis set consisting of 256 GTFs reported by Maroulis.¹⁹ KT3, KT4, and PA1 basis sets were built up adding Maroulis's optimized GTFs (Ref. 19) upon strong substrates. The first substrate is an uncontracted set of ($10s6p3d/7s3p$) GTFs from the atomic natural orbitals basis set ANO-S.²⁰ The second substrate is a larger uncontracted set of ($14s9p4d3f/8s4p3d$) GTFs from the atomic natural orbitals basis set ANO-L.^{21,22} Exponents for ($10s6p3d/7s3p$) and ($14s9p4d3f/8s4p3d$) substrates can be found in Ref. 23. Finally, PA2 and PA3 basis sets were built up adding additional GTFs upon PA basis set¹⁹ in an even-tempered way. Five and seven membered d and f GTFs were used in all cases. The composition of KT3, KT4, PA1, PA2, and PA3 basis sets are as follows (exponents in a_0^{-2}):

$$\begin{aligned} \text{KT3} = & (10s6p3d/7s3p) + (\text{O}:s = 0.077\ 33, 0.028\ 74, \\ & p = 0.053\ 02, 0.018\ 98, d = 2.960\ 93, 1.103\ 88, \\ & 0.411\ 54, 0.153\ 43, \\ & 0.057\ 20, 0.021\ 33, f = 1.103\ 88, \\ & 0.411\ 54, 0.153\ 43, 0.057\ 20/\text{H}: \\ & s = 0.031\ 302, 0.010\ 891, \\ & p = 1.781\ 94, 0.779\ 04, 0.148\ 90, 0.065\ 10, \\ & 0.028\ 46, d = 0.779\ 04, 0.148\ 90, \\ & 0.065\ 10, f = 0.779\ 04, 0.148\ 90), \end{aligned}$$

$$\begin{aligned} \text{KT4} = & (14s9p4d3f/8s4p3d) + (\text{O}:s = 0.028\ 74, \\ & p = 0.018\ 98, d = 0.057\ 20, 0.021\ 33, \\ & f = 0.153\ 43, 0.057\ 20/\text{H}:s = 0.010\ 891, \\ & p = 1.781\ 94, 0.148\ 90, 0.065\ 10, 0.028\ 46, \\ & d = 0.148\ 90, 0.065\ 10, f = 0.779\ 04, 0.148\ 90), \end{aligned}$$

$$\begin{aligned} \text{PA1} = & (14s9p4d3f/8s4p3d) \\ & + (\text{O}:s = 0.072\ 459, 0.028\ 849, 0.011\ 486, \\ & 0.004\ 573, p = 0.046\ 088, 0.018\ 642, 0.007 \\ & 54, 0.003\ 05, d = 1.8040, 1.0930, 0.6622, 0.4012, \\ & 0.2431, 0.1473, 0.0541, 0.0199, \\ & f = 1.0930, 0.4012, 0.2431, 0.1473, 0.0541/\text{H}: \\ & s = 0.028\ 054\ 80, 0.011\ 753\ 50, 0.004\ 924\ 10, \end{aligned}$$

$$\begin{aligned} p = & 1.8303, 1.1948, 0.7799, 0.3323, \\ & 0.1416, 0.0603, 0.0257, d = 0.7799, 0.1416, 0.0603, \\ & f = 0.7799, 0.1416), \end{aligned}$$

$$\begin{aligned} \text{PA2} = & \text{PA} + (\text{O}:d = 2.977\ 507, 0.089\ 246, \\ & f = 0.089\ 246, g = 0.4012, 0.2431, 0.1473/\text{H}: \\ & p = 2.803\ 814, 0.509\ 046, d = 0.509\ 046), \end{aligned}$$

$$\begin{aligned} \text{PA3} = & \text{PA} + (\text{O}:d = 2.977\ 507, 0.089\ 246, \\ & f = 0.089\ 246, g = 0.4012, 0.2431, 0.1473/\text{H}: \\ & p = 2.803\ 814, 0.509\ 046, d = 1.830\ 300, \\ & 0.509\ 046, f = 1.830\ 300). \end{aligned}$$

The electron correlation corrections for the dipole polarizability were evaluated via coupled cluster (CC) techniques. Suitable presentations of these tools and their applications for predicting molecular properties are available in standard textbooks.^{24,25} In this work, all molecular orbitals were accessible in post-Hartree-Fock calculations.

The GAUSSIAN98 (Ref. 26) and DALTON (Ref. 27) packages were employed in the present calculations to obtain *ab initio* dipole polarizabilities. Two different methods were used. As first alternative, we have used the orbital-relaxed finite field method^{28,29} implemented in GAUSSIAN98 and DALTON, where the molecule is perturbed by external homogeneous electric fields of strength $\pm 0.0050e^{-1}a_0^{-1}E_h$ and $\pm 0.0075e^{-1}a_0^{-1}E_h$. Thus, the static dipole polarizabilities are determined as the numerical second derivatives of the total electronic perturbed energy with respect to the strength of the external electric field. In the orbital-relaxed finite field method the electric perturbation is included in the calculation of both the self-consistent-field (SCF) reference state and the CC contribution. As second alternative, we have used the linear response function for coupled cluster wave functions³⁰ implemented in DALTON. Response functions describe how an observable represented by an hermitian operator responds to a time-dependent field. The response can be linear in the field, in which case we have the linear response function. If the operator is the electric dipole operator and the time-dependent field is a periodic electrical field then the linear response function is the dynamic dipole polarizability. It is important to stress that CC linear response dipole polarizabilities in the frequency-independent limit (at $\lambda = \infty$) coincide with the orbital-unrelaxed finite field result,²⁷ where the perturbation of the external electric field is only included in the CC part of the *ab initio* calculation.

The *ab initio* dipole polarizabilities presented here are always referred to a molecule-fixed xyz axis system with origin at the oxygen atom. The x and z axes are contained in the molecular plane, where the x axis bisects the bond angle ϕ and the z axis points toward H atom numbered as 1 (Ref. 31) (see Fig. 1). Dipole polarizability is independent of the origin, even for ions.³² The dependence of the Cartesian components α_{mn} of the dipole polarizability was expressed as a power series in the symmetry *curvilinear* displacements

$$\Delta S_1 = (\Delta R_1 + \Delta R_2)/\sqrt{2}, \quad (1)$$

FIG. 1. Reference axis system and phases of symmetry curvilinear coordinates. xz is the molecular symmetry plane and the x axis bisects the ϕ angle. I' representation, customarily used for prolate top molecules (Ref. 31).

$$\Delta S_2 = d\Delta\phi, \quad (2)$$

$$\Delta S_3 = (\Delta R_2 - \Delta R_1)/\sqrt{2}, \quad (3)$$

$$\alpha_{mn} = \sum_i \sum_j \sum_k \alpha_{mn}^{ijk} \Delta S_1^i \Delta S_2^j \Delta S_3^k,$$

$$m, n = x, y, z, \quad 0 \leq i + j + k \leq N, \quad (4)$$

where ΔR_1 , ΔR_2 , and $\Delta\phi$ are measured with respect to the reference geometry $R_1^0 = R_2^0 = 0.95843 \text{ \AA}$ and $\phi^0 = 104.44^\circ$, and $d = 1 \text{ \AA}$ is a normalization length. The coefficients α_{mn}^{ijk} were determined by a least-squares fit to the calculated *ab initio* grid of α_{nm} . N is the order of the fit. In the C_{2v} group, ΔS_1 , ΔS_2 , α_{xx} , α_{yy} , and α_{zz} are of A_1 symmetry; α_{xz} and ΔS_3 are of B_1 symmetry.³³

In addition to the Cartesian components we compute also the mean, $\bar{\alpha}$, and the anisotropy, $\Delta\alpha$, of the dipole polarizability, defined for symmetric tensors as

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3, \quad (5)$$

$$\Delta\alpha = (1/2)^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)]^{1/2}. \quad (6)$$

In order to compare our results with previous work, we have calculated the Raman intensities for the fundamental vibrational bands of H₂O molecule. They are defined by the intensity activity coefficient I ,

$$I = (45\bar{\alpha}'^2 + 7\Delta\alpha'^2), \quad (7)$$

and the depolarization ratio ρ ,

$$\rho = \frac{3\gamma'^2}{(45\bar{\alpha}'^2 + 4\Delta\alpha'^2)}. \quad (8)$$

$\bar{\alpha}'$ and $\Delta\alpha'^2$ are expressed as

$$\bar{\alpha}' = \frac{1}{3} \left[\left(\frac{\partial \alpha_{xx}}{\partial Q_i} \right)_{\text{eq}} + \left(\frac{\partial \alpha_{yy}}{\partial Q_i} \right)_{\text{eq}} + \left(\frac{\partial \alpha_{zz}}{\partial Q_i} \right)_{\text{eq}} \right], \quad (9)$$

$$\Delta\alpha'^2 = \frac{1}{2} \left[\left(\frac{\partial \alpha_{xx}}{\partial Q_i} - \frac{\partial \alpha_{yy}}{\partial Q_i} \right)_{\text{eq}}^2 + \left(\frac{\partial \alpha_{yy}}{\partial Q_i} - \frac{\partial \alpha_{zz}}{\partial Q_i} \right)_{\text{eq}}^2 + \left(\frac{\partial \alpha_{zz}}{\partial Q_i} - \frac{\partial \alpha_{xx}}{\partial Q_i} \right)_{\text{eq}}^2 \right] + 3 \left[\left(\frac{\partial \alpha_{xy}}{\partial Q_i} \right)_{\text{eq}}^2 + \left(\frac{\partial \alpha_{xz}}{\partial Q_i} \right)_{\text{eq}}^2 + \left(\frac{\partial \alpha_{yz}}{\partial Q_i} \right)_{\text{eq}}^2 \right], \quad (10)$$

where $(\partial \alpha_{nm} / \partial Q_i)_{\text{eq}}$ are the first derivatives of the Cartesian components of the dipole polarizability at the equilibrium

TABLE I. Self-consistent-field values for the static dipole polarizability of H₂O.

Basis set	α_{xx}	α_{yy}	α_{zz}
$R_{\text{OH}} = 0.95843 \text{ \AA}$ and $\phi = 104.44^\circ$			
aug-cc-pVDZ	8.0649	7.3282	9.0551
aug-cc-pVTZ	8.3987	7.7266	9.1822
aug-cc-pVQZ	8.4968	7.8506	9.2017
aug-cc-pV5Z	8.5233	7.8828	9.2019
aug-cc-pV6Z	8.5314	7.8962	9.2033
W ₆	8.5392	7.8945	9.2019
$R_{\text{OH}} = 0.79843 \text{ \AA}$ and $\phi = 74.44^\circ$			
aug-cc-pVDZ	6.5506	6.5882	6.3591
aug-cc-pVTZ	6.7412	6.9167	6.4779
aug-cc-pVQZ	6.7992	6.9917	6.4969
aug-cc-pV5Z	6.8140	7.0104	6.4971
aug-cc-pV6Z	6.8186	7.0170	6.4985
W ₆	6.8241	7.0140	6.4977
$R_{\text{OH}} = 1.11843 \text{ \AA}$ and $\phi = 134.44^\circ$			
aug-cc-pVDZ	9.1221	8.1242	14.4282
aug-cc-pVTZ	9.6855	8.7401	14.5577
aug-cc-pVQZ	9.8913	8.9632	14.5780
aug-cc-pV5Z	9.9506	9.0260	14.5813
aug-cc-pV6Z	9.9754	9.0552	14.5825
W ₆	9.9960	9.0707	14.5807
$R_{\text{OH}} = 1.20000 \text{ \AA}$ and $\phi = 180^\circ$			
aug-cc-pVDZ	8.7185	8.7185	18.0821
aug-cc-pVTZ	9.6145	9.6145	18.2554
aug-cc-pVQZ	10.0518	10.0518	18.2857
aug-cc-pV5Z	10.1867	10.1867	18.2826
aug-cc-pV6Z	10.2609	10.2609	18.2845
W ₆	10.3388	10.3388	18.2866

geometry with respect to the mass-weighted normal mode coordinate Q_i associated to the fundamental frequency ω_i . In this approximation, the contributions to vibrational Raman intensities from higher derivatives of α_{nm} with respect to the normal mode coordinates and rotation-vibration coupling are neglected.

III. RESULTS

A. Dipole polarizability surfaces

The calculations were initiated by a basis set convergence study of the SCF static dipole polarizability at four C_{2v} symmetry geometries: (1°) $R_1 = R_2 = 0.95843 \text{ \AA}$ and $\phi = 104.44^\circ$; (2°) $R_1 = R_2 = 0.79843 \text{ \AA}$ and $\phi = 74.44^\circ$; (3°) $R_1 = R_2 = 1.11843 \text{ \AA}$ and $\phi = 134.44^\circ$; (4°) $R_1 = R_2 = 1.20000 \text{ \AA}$ and $\phi = 180^\circ$. The results are given in Table I using the correlation-consistent basis sets aug-cc-pVXZ ($X = \text{D, T, Q, 5, 6}$) developed by Dunning *et al.*³⁴ and the W₆ basis set. The closeness of the present SCF/W₆ values of the static dipole polarizability to the Hartree-Fock limit is evident. Accordingly, we can conclude that W₆ basis set quality does not seem to vary for large nuclear displacements from the equilibrium geometry.

The second step was a study about electron correlation effects. In Table II we present linear response CCSD/W₆ and orbital-relaxed finite field CCSD(T)/W₆ static dipole polar-

TABLE II. ΔS_1 (Å), ΔS_2 (deg Å), and ΔS_3 (Å), Eqs. (1)–(3), dependence of the CCSD/ W_6 linear response and the CCSD(T)/ W_6 orbital-relaxed finite field static dipole polarizability.

ΔS_1	ΔS_2	ΔS_3	CCSD/ W_6				CCSD(T)/ W_6			
			α_{xx}	α_{yy}	α_{zz}	α_{xz}	α_{xx}	α_{yy}	α_{zz}	α_{xz}
−0.339	−20.000	−0.339	7.186	7.527	6.592	−1.489	7.167	7.522	6.565	−1.480
−0.339	20.000	−0.339	7.238	7.772	6.894	−1.116	7.228	7.766	6.864	−1.113
−0.339	−30.000	−0.113	6.679	7.537	6.313	−0.513	6.658	7.538	6.292	−0.509
−0.226	−10.000	−0.226	7.815	8.145	7.396	−1.169	7.795	8.141	7.365	−1.163
−0.226	10.000	−0.226	7.843	8.284	7.628	−1.020	7.830	8.280	7.594	−1.016
−0.226	0.000	−0.113	7.670	8.220	7.336	−0.550	7.653	8.217	7.305	−0.547
−0.113	−30.000	−0.339	9.648	8.627	8.452	−2.235	9.610	8.621	8.418	−2.222
−0.113	30.000	−0.339	8.946	9.045	9.739	−1.474	8.931	9.033	9.691	−1.474
0.000	−30.000	−0.339	10.962	9.169	9.600	−2.597	10.913	9.163	9.562	−2.586
0.000	30.000	−0.339	9.801	9.646	11.692	−1.828	9.782	9.629	11.638	−1.832
0.000	0.000	0.000	9.631	9.329	9.990	0.000	9.600	9.324	9.941	0.000
0.000	40.000	0.000	9.757	9.828	10.944	0.000	9.741	9.816	10.874	0.000
0.113	−30.000	−0.339	12.351	9.706	10.893	−2.951	12.291	9.693	10.853	−2.944
0.113	30.000	−0.339	10.713	10.253	14.118	−2.254	10.685	10.226	14.064	−2.265
0.226	0.000	−0.113	12.059	10.475	13.984	−1.104	12.002	10.457	13.913	−1.103
0.226	−10.000	−0.226	12.562	10.362	13.498	−2.240	12.501	10.348	13.441	−2.240
0.226	10.000	−0.226	11.931	10.575	14.884	−2.114	11.883	10.553	14.815	−2.117
0.339	−30.000	−0.113	14.563	10.788	13.984	−1.242	14.448	10.766	13.923	−1.245
0.339	−20.000	−0.339	14.702	10.807	14.762	−3.609	14.640	10.773	14.720	−3.634
0.339	20.000	−0.339	12.871	11.252	19.145	−3.414	12.806	11.198	19.100	−3.445

izabilities at different geometries. These calculations point that linear response CCSD and orbital-relaxed finite field CCSD(T) results are close within 0.8%, although this coincidence cannot be extrapolated to other molecules. In Table III we show an analysis of electron correlation corrected values at the experimental equilibrium geometry, $R_1=R_2=0.9572$ Å and $\phi=104.52^\circ$, using different coupled-cluster models with W_6 , PA, and KT4 basis sets. It must be noticed that orbital-unrelaxed CCSD and CCSD(T) static values are also close within 0.8%. At the same time, it is also observed in Table III that a higher quality coupled-cluster model than CCSD and CCSD(T) such as CC3 yields larger dipole polarizabilities employing the orbital-relaxed finite field method. Spelsberg and Meyer³⁵ reported both static and dynamic at $\lambda=514.5$ nm values calculated with the single-excitation

TABLE III. Electron correlation corrected values of the static dipole polarizability of H_2O with W_6 , PA (Ref. 19), and KE4 basis sets at the experimental geometry $R_1=R_2=0.9572$ Å and $\phi=104.52^\circ$.

	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
CCSD/ W_6^a	9.6130	9.3212	9.9673	9.634	0.560
CCSD(T)/ W_6^b	9.6721	9.3904	10.0196	9.694	0.546
CCSD/ W_6^c	9.3646	9.0448	9.7579	9.389	0.619
CCSD(T)/ W_6^c	9.5821	9.3161	9.9183	9.606	0.523
CC3/ W_6^c	9.6440	9.3902	9.9610	9.665	0.495
CCSD(T)/PA ^c	9.5706	9.3126	9.9110	9.598	0.520
CC3/PA ^c	9.6321	9.3876	9.9537	9.658	0.492
CCSD(T)/KT4 ^c	9.5578	9.2912	9.9006	9.583	0.529
CC3/KT4 ^c	9.6153	9.3624	9.9386	9.639	0.500

^aLinear response calculation.^bOrbital-unrelaxed finite field calculation.^cOrbital-relaxed finite field calculation.

multireference CI (SE-MRCI) model, and static values for a large number of correlation methods provided by the MOLPRO program suite. They used a medium size basis set ($14s10p5d4f1g/13s4p3d$) at a molecular geometry obtained by averaging over the zero-point vibration, $R_1=R_2=0.9724$ Å and $\phi=104.63^\circ$. Their theoretical predictions are presented with ours in Table IV. From a comparison of the CCSD(T) results in Table IV, we can conclude that both ($14s10p5d4f1g/13s4p3d$) and W_6 basis sets have a similar quality. For this reason, the *ab initio* calculations published by Spelsberg and Meyer³⁵ help us as a guide about the accuracy of the electron correlation corrections obtained with the CCSD model and linear response theory.

The third step was a study about basis set truncation effects. With this intention, we have calculated orbital-relaxed finite field static dipole polarizabilities using the CCSD(T) model with POL1,³⁶ uncontracted Nasa-ames-ANO ($13s8p6d4f2g/8s6p4d3f$),³⁷ aug-cc-pVXZ ($X=D,T,Q,5$),³⁴ daug-cc-pVXZ ($X=D,T,Q,5$),³⁴ KT3, KT4 PA, PA1, PA2, and PA3 basis sets. The results are shown in Table V. It should be noticed that the aug-cc-pV5Z basis set yields a lower electron correlation correction than the PA1 and KE4 basis sets although its SCF values are close to the Hartree–Fock limit, Table I. This would explain the too low theoretical estimation for the mean dipole polarizability $\bar{\alpha}=9.3$ suggested by Feller.³⁸ Another conclusion from Table V is that aug-cc-pVXZ ($X=D,T,Q,5$) and daug-cc-pVXZ ($X=D,T,Q,5$) series converge to neither similar dipole polarizabilities nor the values obtained with KT4 and PA1 basis sets. On the other hand, the CCSD(T) static dipole polarizabilities calculated with W_6 and PA basis sets are similar because they were designed following the successful computational philosophy explained by Maroulis^{18,19,39,40} for ob-

TABLE IV. Comparison of theoretical predictions for static and dynamic at 514.5 nm dipole polarizability of H₂O. $R_1=R_2=0.9724$ Å and $\phi=104.63^\circ$ (averaged zero-point geometry).

	$\lambda=\infty$					$\lambda=514.5$ nm				
	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
CCSD ^a	9.82	9.43	10.29	9.85	0.75	10.10	9.81	10.51	10.14	0.61
SE-MRCI ^c	9.72	9.30	10.29	9.77	0.86	9.97	9.65	10.51	10.04	0.75
CCSD(T) ^c	9.76	9.40	10.22	9.79	0.71					
CCSD(T) ^b	9.79	9.42	10.23	9.81	0.70					
CAS-CI ^c	9.66	9.22	10.17	9.68	0.82					
CAS-ACPF ^c	9.77	9.23	10.22	9.74	0.86					
MP4(SDQ) ^c	9.62	9.19	10.12	9.64	0.81					

^aThis work, linear response calculation.^bThis work, orbital-relaxed finite field calculation.^cSpelsberg *et al.* (Ref. 35).

taining static dipole polarizabilities of Hartree–Fock quality. However, the dipole polarizabilities obtained with these two basis sets W₆ and PA are a little larger than those calculated with KT4 and PA1 basis sets since they can generate an electronic distribution too diffuse. It can also be observed in Table V that when we proceed to saturate PA basis set, as we have done with PA2 and PA3 basis sets, dipole polarizabilities begin to decrease to the values obtained with PA1 and KT4 basis sets. Finally, from the calculations presented in Table V we can state that well calibrated basis sets are needed to obtain accurate *ab initio* dipole polarizability surfaces with an acceptable computational effort; e.g., daug-cc-pV5Z basis set would be an excellent choice but it has 373 contracted GTFs and it is not practical for calculating the α and $\alpha(514.5$ nm) surfaces for the time being. Moreover, basis sets just optimized for ground electronic energies may lead to rather poor dipole polarizabilities; see the results obtained with the uncontracted Nasa-Ames-ANO basis set in Table V.

As conclusion from this study about electron correlation and basis set truncation effects, our linear response dipole polarizabilities calculated at the CCSD/W₆ level of theory decrease slightly if we saturate well calibrated basis sets like PA and increase slightly if we take into account high-level electron correlation effects beyond the CCSD model: see Table III. For these two reasons, and considering the results reported by Spelsberg and Meyer³⁵ with sophisticated correlation models, there exists probably a cancellation of electron correlation and basis set truncation errors. This circumstance would mean that our linear response CCSD/W₆ dipole polarizability values are close to the full-CI/CBS limit within 4%. Thus, the mean polarizabilities and anisotropies calculated at this level of theory could be accurate to $\pm 2\%$ and $\pm 10\%$, respectively.

The last step in our *ab initio* calculations was to obtain the linear response CCSD/W₆ dipole polarizability surfaces of water molecule at $\lambda=\infty$ (zero frequency), α , and at $\lambda=514.5$ nm, $\alpha(514.5$ nm), in a grid of 521 points along the

TABLE V. CCSD(T) energies and orbital-relaxed finite field values of the static dipole polarizability of H₂O with POL1 (Ref. 36), Nasa-Ames-ANO (Ref. 37), aug-cc-pVXZ ($X=D, T, Q, 5$) (Ref. 34), daug-cc-pVXZ ($X=D, T, Q, 5$) (Ref. 34), KT3, KT4, W₆, PA (Ref. 19), PA1, PA2, and PA3 basis sets. $R_1=R_2=0.95843$ Å and $\phi=104.44^\circ$.

Basis set	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	Energy
POL1	9.6629	9.4335	10.0565	9.718	0.546	−76.294 439 2
Nasa-Ames-ANO ^a	9.4120	8.9902	9.8461	9.416	0.741	−76.425 976 9
aug-cc-pVDZ	8.9761	8.6097	9.8077	9.131	1.063	−76.276 043 7
aug-cc-pVTZ	9.3708	9.0391	9.9093	9.440	0.761	−76.357 530 5
aug-cc-pVQZ	9.4656	9.1532	9.8874	9.502	0.638	−76.395 257 0
aug-cc-pV5Z	9.4890	9.1782	9.8705	9.513	0.601	−76.408 935 7
daug-cc-pVDZ	9.6056	9.4698	9.9918	9.689	0.469	−76.277 014 6
daug-cc-pVTZ	9.5901	9.3450	9.9494	9.628	0.527	−76.358 177 4
daug-cc-pVQZ	9.5416	9.2572	9.8990	9.566	0.557	−76.395 508 1
daug-cc-pV5Z	9.5398	9.2251	9.8796	9.548	0.567	−76.409 091 9
W ₆	9.6000	9.3241	9.9413	9.622	0.536	−76.381 166 4
KT3	9.5853	9.3156	9.9317	9.611	0.535	−76.399 236 8
PA	9.5880	9.3208	9.9336	9.614	0.532	−76.405 095 5
PA2	9.5824	9.3129	9.9278	9.608	0.534	−76.410 126 2
PA3	9.5726	9.3039	9.9168	9.598	0.532	−76.412 215 2
KT4	9.5690	9.2918	9.9190	9.593	0.544	−76.414 428 1
PA1	9.5635	9.2826	9.9137	9.587	0.548	−76.416 505 6

^aUncontracted (13s8p6d4f2g/8s6p4d3f) basis set.

TABLE VI. Fitted coefficients α_{mn}^{ijk} of Eq. (4) up to $i+j+k=4$ for the diagonal Cartesian components of the *ab initio* linear response dipole polarizability of H₂O at the CCSD/W₆ level of theory.

$i\ j\ k$	$\lambda=\infty$			$\lambda=514.5\text{ nm}$			Units
	α_{xx}^{ijk}	α_{yy}^{ijk}	α_{zz}^{ijk}	α_{xx}^{ijk}	α_{yy}^{ijk}	α_{zz}^{ijk}	
0 0 0	1.587 87	1.538 18	1.647 20	1.631 33	1.598 84	1.681 67	$10^{-40}\text{ CV}^{-1}\text{ m}^2$
0 1 0	-0.076 14	0.083 61	0.247 30	-0.060 44	0.088 66	0.253 30	$10^{-30}\text{ CV}^{-1}\text{ m}$
1 0 0	1.607 10	0.828 63	2.393 94	1.697 39	0.907 06	2.496 18	$10^{-30}\text{ CV}^{-1}\text{ m}$
0 0 2	0.711 19	-0.042 32	0.895 49	0.793 81	-0.031 29	1.005 69	10^{-20} CV^{-1}
0 2 0	0.133 31	0.056 66	0.039 54	0.145 06	0.062 10	0.046 42	10^{-20} CV^{-1}
2 0 0	0.618 42	0.081 72	1.994 83	0.714 38	0.146 58	2.178 92	10^{-20} CV^{-1}
1 1 0	-0.705 21	0.085 57	0.996 80	-0.688 59	0.102 76	1.032 61	10^{-20} CV^{-1}
0 3 0	0.053 28	-0.002 71	-0.089 00	0.055 49	-0.003 25	-0.094 62	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
3 0 0	-0.209 59	-0.118 92	0.536 19	-0.160 34	-0.065 20	0.737 44	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
0 1 2	-1.082 01	-0.069 26	0.965 99	-1.145 51	-0.101 33	1.094 18	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
1 0 2	0.356 24	-0.108 06	0.411 79	0.593 71	-0.046 83	0.768 23	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
1 2 0	0.008 92	0.081 90	-0.082 90	0.028 55	0.106 69	-0.066 18	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
2 1 0	-0.354 95	0.069 99	1.624 67	-0.319 77	0.111 17	1.737 83	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
0 0 4	-0.221 79	-0.058 90	0.042 90	-0.182 52	-0.056 99	0.115 18	$\text{CV}^{-1}\text{ m}^{-2}$
0 4 0	-0.031 82	-0.008 00	-0.022 03	-0.034 86	-0.008 47	-0.022 22	$\text{CV}^{-1}\text{ m}^{-2}$
4 0 0	-0.517 09	-0.111 11	-0.629 16	-0.545 66	-0.062 40	-0.514 25	$\text{CV}^{-1}\text{ m}^{-2}$
0 2 2	0.346 44	0.129 95	-0.202 22	0.376 02	0.170 64	-0.161 39	$\text{CV}^{-1}\text{ m}^{-2}$
1 1 2	0.013 74	-0.091 19	3.293 20	-0.034 42	-0.178 70	4.052 48	$\text{CV}^{-1}\text{ m}^{-2}$
2 0 2	-1.259 79	-0.483 61	-2.275 59	-1.027 88	-0.343 93	-1.898 19	$\text{CV}^{-1}\text{ m}^{-2}$
2 2 0	-0.038 25	-0.030 88	0.159 71	0.016 97	0.021 00	0.210 50	$\text{CV}^{-1}\text{ m}^{-2}$
3 1 0	0.183 26	-0.094 11	1.205 26	0.245 90	-0.029 78	1.415 46	$\text{CV}^{-1}\text{ m}^{-2}$
1 3 0	0.174 26	0.059 92	-0.184 05	0.182 96	0.063 93	-0.200 08	$\text{CV}^{-1}\text{ m}^{-2}$

symmetry curvilinear displacements defined by Eqs. (1)–(3), contained within a hypersphere centered around our reference configuration $R_1^0=R_2^0=0.958\,43\text{ \AA}$, $\phi^0=104.44^\circ$. To obtain an accurate description of the dipole polarizability surface valid for large amplitude motions of the nuclei, ΔS_1 and ΔS_3 were varied between $-0.452\,55\text{ \AA}$ and $+0.452\,55\text{ \AA}$ and $\Delta\phi$ between -50° and $+70^\circ$. The Cartesian dipole polarizability coefficients according to Eq. (4) are given in Tables VI and VII. The standard deviations of the least-squares fits of α_{mn} were $<10^{-4}$.

B. Comparison with experimental data

In order to compare properly our theoretical predictions with experimental data we need to have accurate rovibra-

tional wave functions for H₂O, D₂O, and HDO molecules. They have been calculated from the diagonalization of a complete rovibrational Hamiltonian^{41,42} using the isotope dependent potentials of Partridge and Schwenke,⁴³ more details can be found in previous work.^{14,15} With these wave functions and the $\alpha(514.5\text{ nm})$ surface calculated at the CCSD/W₆ level of theory we have reproduced satisfactorily all the experimental data of the molecular polarizability of water molecule available to date: (i) absolute value of the dynamic at 514.5 nm mean dipole polarizability $\bar{\alpha}(514.5\text{ nm})=10.343$ (obtained from the molar refractivity⁴⁴ at low temperature and zero density), (ii) depolarization ratio $\rho=(2.99\pm0.45)\times10^{-4}$ and coefficient $R_{20}=0.75\pm0.05$ of the rotational Raman spectrum of H₂O,⁴⁵ (iii) rotational Raman

TABLE VII. Fitted coefficients α_{mn}^{ijk} of Eq. (4) up to $i+j+k=4$ for the *xz* Cartesian component of the *ab initio* linear response dipole polarizability of H₂O at the CCSD/W₆ level of theory.

$i\ j\ k$	$\lambda=\infty$	$\lambda=514.5\text{ nm}$	Units
	α_{xz}^{ijk}	α_{xz}^{ijk}	
0 0 1	1.179 04	1.243 22	$10^{-30}\text{ CV}^{-1}\text{ m}$
0 1 1	-0.377 00	-0.369 18	10^{-20} CV^{-1}
1 0 1	1.855 59	2.068 01	10^{-20} CV^{-1}
0 0 3	0.006 98	0.088 04	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
0 2 1	-0.360 99	-0.354 36	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
1 1 1	-0.002 02	0.080 85	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
2 0 1	0.620 70	0.935 18	$10^{-10}\text{ CV}^{-1}\text{ m}^{-1}$
0 1 3	0.530 70	0.605 96	$\text{CV}^{-1}\text{ m}^{-2}$
1 0 3	-0.642 52	-0.440 15	$\text{CV}^{-1}\text{ m}^{-2}$
1 2 1	-0.634 96	-0.581 08	$\text{CV}^{-1}\text{ m}^{-2}$
0 3 1	-0.128 23	-0.140 33	$\text{CV}^{-1}\text{ m}^{-2}$
2 1 1	1.403 56	1.714 45	$\text{CV}^{-1}\text{ m}^{-2}$
3 0 1	-1.240 44	-1.087 51	$\text{CV}^{-1}\text{ m}^{-2}$

TABLE VIII. Comparison of experimental and theoretical Raman intensity activity coefficients ($\text{\AA}^4/\text{u.a.m}$) and depolarization ratios (in parentheses) of ν_2 , ν_1 , and ν_3 vibrational bands of the H₂O molecule calculated at different levels of theory.

		$\lambda = \infty$				$\lambda = 514.5 \text{ nm}$	
Frequency ^a (cm ⁻¹)		SCF ^b	CCSD ^b	C1 ^c	KS-DFT ^d	CCSD ^e	Expt. ^f
ν_2	1594.746	1.0(0.75)	1.0(0.71)	1.1	1.0(0.59)	0.8(0.71)	$ 0.9 \pm 2 (0.74)$
ν_1	3657.053	88(0.06)	111(0.04)	102	111(0.04)	119(0.04)	$108 \pm 14(0.03)$
ν_3	3755.929	25(0.75)	26(0.75)	31	25(0.75)	28(0.75)	$19.2 \pm 2.1(0.75)$

^aExperimental frequencies by Tennyson *et al.* (Ref. 46).

^bPOL1 basis set (Ref. 36), Perera and Barlett (Ref. 49).

^c[5s4pd/5s1p] basis set, John, Backsay, and Hush (Ref. 47).

^dVTZP+ basis set, Stirling (Ref. 48).

^eW₆ basis set.

^fFrom the dipole polarizability derivatives estimated by Murphy (Refs. 50 and 51).

spectra of H₂O, D₂O, and HDO,¹⁴ (iv) rotational-vibrational Raman spectra of the ν_2 band of H₂O, D₂O, and HDO,¹⁵ and (v) rotational-vibrational Raman spectra of the $2\nu_2$ and ν_1/ν_3 bands of H₂O, D₂O and HDO.¹⁶

The calculated magnitudes of the CCSD/W₆ dipole polarizability at $\lambda=514.5 \text{ nm}$ vibrationally averaged for the ground state of H₂O are $\rho=3.28 \times 10^{-4}$, $R_{20}=0.70$, and $\bar{\alpha}(514.5 \text{ nm})=10.243$ and they compare well with the experimental ones. The same values have been calculated previously with the $\alpha(514.5 \text{ nm})$ surface at the CCSD/aug-cc-pVQZ level of theory, but the results were less satisfactory, yielding $\rho=4.69 \times 10^{-4}$, $R_{20}=0.68$, and $\bar{\alpha}(514.5 \text{ nm})=10.089$. This example further illustrate the sensitivity of the dipole polarizability with respect to basis set quality.

The dipole polarizability surface beyond the “equilibrium” geometry has been tested through the vibrational Raman spectrum, points (iv) and (v) above. The depolarization ratios of the ν_1 and ν_3 vibrational Raman bands of H₂O, D₂O, and HDO proved especially difficult to reproduce because they are very sensitive to small changes of the Cartesian components of the dipole polarizability derivatives relative to each others. The CCSD/W₆ $\alpha(514.5 \text{ nm})$ surface was able to reproduce all the rovibrational Raman spectra of the isotopic species H₂O, D₂O, and HDO, including depolarization ratios. Previous attempts employing Møller–Plesset perturbation theory with the aug-cc-pVTZ and aug-cc-pVQZ basis sets failed to reproduce them with the same precision. It must be stressed that the simulation of the rotation-vibration Raman spectra is a very tough test. These spectra consist of hundreds of transitions for H₂O at room temperature and correspondingly more for D₂O and HDO,^{14–16} while the intensities spread over two orders of magnitude.

We have also calculated the Raman intensities and depolarization ratios, Eqs. (9) and (10), of the ν_2 , ν_1 , and ν_3 vibrational bands of H₂O molecule using the $\alpha(514.5 \text{ nm})$ surface at the CCSD/W₆ level of theory. Mass-weighted normal mode coordinates were obtained from a GF analysis for the H₂O potential of Partridge and Schwenke.⁴³ These intensities and the experimental frequencies⁴⁶ are presented in Table VIII. They are also compared with theoretical predictions at different levels of theory^{47–49} and the experimental estimations determined by Murphy.^{50,51} The discrepancy between the theoretical predictions and the experimental esti-

mation of the total Raman scattering cross section of ν_3 vibrational band has been discussed in Ref. 16 in some detail.

IV. VIBRATIONAL AVERAGES

We have calculated the vibrational averages to the dipole polarizability for the six lowest energy vibrational states of H₂O, D₂O, and HDO molecules. The vibrational average of a molecular property P may be determined from its expectation value

$$\langle P \rangle = \langle \Phi | P | \Phi \rangle = P_e + \langle P \rangle^{\text{ZPVC}} = P_e + \langle P \rangle_H^{\text{ZPVC}} + \langle P \rangle_A^{\text{ZPVC}}, \quad (11)$$

for the vibrational wave function $\Phi = c_0 \Phi_0 + c' \Phi'$, where Φ_0 is the main harmonic contribution to Φ . P_e is the value of P at the equilibrium geometry, $\langle P \rangle^{\text{ZPVC}}$ is the zero-point vibrational correction of the Φ wave function to P . $\langle P \rangle_H^{\text{ZPVC}} = \langle \Phi_0 | P - P_e | \Phi_0 \rangle$ is the ZPVC due to the harmonic part of wave function (mechanical harmonicity) while $\langle P \rangle_A^{\text{ZPVC}} = \langle P \rangle - P_e - \langle P \rangle_H^{\text{ZPVC}}$ is the ZPVC due to the anharmonic part of the wave function (mechanical anharmonicity). The zero vibrational point corrections $\langle P \rangle_H^{\text{ZPVC}}$ calculated in this work are not null since our dipole polarizability surfaces contain second and higher derivatives of α and $\alpha(514.5 \text{ nm})$ with respect to the normal mode coordinates. The vibrational wave functions of the nonrotating molecule, obtained from the diagonalization of the Watson Hamiltonian⁴¹ at $J=0$ using the isotope dependent potentials of Partridge and Schwenke,⁴³ are denoted here by $|v_{J=0}\rangle$ with $v=0, 1, 2, \dots$ increasing in energy. The six lowest vibrational wave functions of H₂O, D₂O, and HDO are expanded in the harmonic basis set $|v_1, v_2, v_3\rangle$ like:

H₂O

$$|0_{J=0}\rangle(0.000 \text{ cm}^{-1}) \approx +0.9869|0,0,0\rangle - 0.1509|1,0,0\rangle, \quad (12)$$

$$|1_{J=0}\rangle(1594.777 \text{ cm}^{-1}) \approx +0.9896|0,1,0\rangle - 0.1209|1,1,0\rangle, \quad (13)$$

$$|2_{J=0}\rangle(3151.625 \text{ cm}^{-1}) \approx +0.9761|0,2,0\rangle + 0.2694|2,0,0\rangle, \quad (26)$$

$$+ 0.1357|1,0,0\rangle, \quad (14)$$

$$|3_{J=0}\rangle(3657.041 \text{ cm}^{-1}) \approx +0.1530|0,0,0\rangle + 0.1848|1,0,0\rangle$$

$$- 0.1352|0,2,0\rangle - 0.1044|0,0,1\rangle, \quad (27)$$

$$+ 0.9125|1,0,0\rangle$$

$$- 0.3111|2,0,0\rangle - 0.1055|0,0,2\rangle, \quad (15)$$

$$|4_{J=0}\rangle(3707.471 \text{ cm}^{-1}) \approx +0.1036|0,2,0\rangle$$

$$+ 0.9319|0,0,1\rangle$$

$$+ 0.1151|1,0,1\rangle + 0.2774|0,0,2\rangle, \quad (28)$$

$$|4_{J=0}\rangle(3755.947 \text{ cm}^{-1}) \approx +0.9431|0,0,1\rangle$$

$$- 0.3019|1,0,1\rangle, \quad (16)$$

$$|5_{J=0}\rangle(4666.787 \text{ cm}^{-1}) \approx +0.1069|0,2,0\rangle - 0.1084|0,4,0\rangle$$

$$+ 0.9395|0,3,0\rangle + 0.7225|1,1,0\rangle$$

$$- 0.1723|0,4,0\rangle + 0.1943|2,1,0\rangle$$

$$+ 0.2190|1,1,0\rangle. \quad (17)$$

$$+ 0.1167|0,1,1\rangle. \quad (29)$$

D₂O,

$$|0_{J=0}\rangle(0.000 \text{ cm}^{-1}) \approx +0.9904|0,0,0\rangle - 0.1300|1,0,0\rangle, \quad (18)$$

$$|1_{J=0}\rangle(1178.411 \text{ cm}^{-1}) \approx +0.9925|0,1,0\rangle + 0.1034|1,1,0\rangle, \quad (19)$$

$$|2_{J=0}\rangle(2336.843 \text{ cm}^{-1}) \approx +0.9804|0,2,0\rangle - 0.1376|1,0,0\rangle, \quad (20)$$

$$|3_{J=0}\rangle(2671.655 \text{ cm}^{-1}) \approx -0.1311|0,0,0\rangle + 0.1387|0,2,0\rangle$$

$$+ 0.9335|1,0,0\rangle + 0.2713|2,0,0\rangle, \quad (21)$$

$$|4_{J=0}\rangle(2787.730 \text{ cm}^{-1}) \approx +0.9580|0,0,1\rangle + 0.2650|1,0,1\rangle, \quad (22)$$

$$|5_{J=0}\rangle(3474.305 \text{ cm}^{-1}) \approx +0.9511|0,3,0\rangle + 0.1423|0,4,0\rangle$$

$$- 0.2260|1,1,0\rangle. \quad (23)$$

HDO,

$$|0_{J=0}\rangle(0.000 \text{ cm}^{-1}) \approx +0.9889|0,0,0\rangle + 0.1043|1,0,0\rangle, \quad (24)$$

$$|1_{J=0}\rangle(1403.517 \text{ cm}^{-1}) \approx +0.9911|0,1,0\rangle, \quad (25)$$

$$|2_{J=0}\rangle(2723.661 \text{ cm}^{-1}) \approx -0.1026|0,0,0\rangle - 0.1949|0,2,0\rangle$$

$$+ 0.9275|1,0,0\rangle$$

The vibrational averages of the dipole polarizability for H₂O, D₂O, and HDO molecules have been calculated by means of Gauss–Hermite quadrature and they are reported in Table IX. Both $\langle P \rangle_H^{\text{ZPVC}}$ and $\langle P \rangle_A^{\text{ZPVC}}$ vibrational zero-point corrections are of the same order. For instance, we obtain the following zero-point vibrational corrections of α and $\alpha(514.5 \text{ nm})$ for the ground state $|0_{J=0}\rangle$ of H₂O molecule: $\langle \alpha_{xx} \rangle_H^{\text{ZPVC}} = 0.0990$, $\langle \alpha_{yy} \rangle_H^{\text{ZPVC}} = 0.0292$, $\langle \alpha_{zz} \rangle_H^{\text{ZPVC}} = 0.1388$, $\langle \alpha_{xx} \rangle_A^{\text{ZPVC}} = 0.2111$, $\langle \alpha_{yy} \rangle_A^{\text{ZPVC}} = 0.1056$, $\langle \alpha_{zz} \rangle_A^{\text{ZPVC}} = 0.3146$, $\langle \alpha_{xx}(514.5 \text{ nm}) \rangle_H^{\text{ZPVC}} = 0.1079$, $\langle \alpha_{yy}(514.5 \text{ nm}) \rangle_H^{\text{ZPVC}} = 0.0341$, $\langle \alpha_{zz}(514.5 \text{ nm}) \rangle_H^{\text{ZPVC}} = 0.1506$, $\langle \alpha_{xx}(514.5 \text{ nm}) \rangle_A^{\text{ZPVC}} = 0.2235$, $\langle \alpha_{yy}(514.5 \text{ nm}) \rangle_A^{\text{ZPVC}} = 0.1162$, and $\langle \alpha_{zz}(514.5 \text{ nm}) \rangle_A^{\text{ZPVC}} = 0.3294$. As conclusion of these calculations, it is evident that in order to obtain fair vibrational averages both high quality dipole polarizability derivatives and wave functions are required.

It is interesting to compare in Table X the vibrational averages of the static dipole polarizability for the vibrational ground state presented here for H₂O molecule with the results obtained by Russell and Spackman,⁵² Rudd, Åstrand, and Taylor,⁵³ and Spelsberg and Meyer.³⁵ Our calculated ZPVCs corrections to the static $\bar{\alpha}$ and $\Delta\alpha$, Eqs. (5) and (6), for H₂O, D₂O, and HDO molecules are compared in Table XI with those reported by Luis *et al.*⁵⁴ at the CPHF/POL1 level of theory. Curiously, the $r = \langle \bar{\alpha} \rangle^{\text{ZPVC}} / \bar{\alpha}_{\text{eq}}$ ratios for H₂O molecule are similar at the CCSD/W₆ ($r = 0.032$), CPHF/POL1 ($r = 0.030$),^{54,55} MP2/POL1 ($r = 0.030$),⁵² and MCSCF/ANO ($r = 0.030$)⁵³ levels of theory, but they are different to the value obtained at the MCSCF (CAS1=4220 configurations)/P3=[8s5p3d1f/4s2p1d] ($r = 0.037$) (Ref. 56) level of theory. Our mean static dipole polarizability averaged for the vibrational ground state of H₂O molecule is $\langle 0_{J=0} | \bar{\alpha} | 0_{J=0} \rangle = 9.94$ and it compares relatively well with the experimental estimation $\bar{\alpha} = 9.83 \pm 0.02$ referenced by Russell and Spackman.⁵² This latter value was obtained from an extrapolation to $\lambda = \infty$ of gas-phase refractive index measurements at different wavelengths less than 900 nm that did not

TABLE IX. Vibrational averages to the *ab initio* linear response CCSD/W₆ dipole polarizability at $\lambda=\infty$ and at $\lambda=514.5$ nm for the six lowest energy vibrational states $|v_J=0\rangle$ of H₂O, D₂O, and HDO molecules. $R_{\text{OH}}^{\text{eq}} \neq R_{\text{DD}}^{\text{eq}}$ in HDO molecule (Ref. 43) and there exists a slight xz contribution for the reference axis system used in this work, Fig. 1.

	$\lambda=\infty$						$\lambda=514.5$ nm					
	$\langle\alpha_{xx}\rangle$	$\langle\alpha_{yy}\rangle$	$\langle\alpha_{zz}\rangle$	$\langle\alpha_{xz}\rangle$	$\langle\bar{\alpha}\rangle$	$\langle\Delta\alpha\rangle$	$\langle\alpha_{xx}\rangle$	$\langle\alpha_{yy}\rangle$	$\langle\alpha_{zz}\rangle$	$\langle\alpha_{xz}\rangle$	$\langle\bar{\alpha}\rangle$	$\langle\Delta\alpha\rangle$
H ₂ O												
$ 0_{J=0}\rangle$	9.932	9.460	10.433	0.000	9.942	0.843	10.217	9.843	10.669	0.000	10.243	0.716
$ 1_{J=0}\rangle$	10.004	9.504	10.516	0.000	10.008	0.876	10.296	9.892	10.756	0.000	10.315	0.749
$ 2_{J=0}\rangle$	10.074	9.549	10.597	0.000	10.073	0.907	10.374	9.941	10.842	0.000	10.386	0.781
$ 3_{J=0}\rangle$	10.210	9.582	10.911	0.000	10.234	1.151	10.515	9.981	11.176	0.000	10.558	1.037
$ 4_{J=0}\rangle$	10.236	9.572	10.833	0.000	10.214	1.093	10.540	9.968	11.094	0.000	10.534	0.975
$ 5_{J=0}\rangle$	10.140	9.595	10.676	0.000	10.137	0.936	10.449	9.991	10.926	0.000	10.455	0.811
D ₂ O												
$ 0_{J=0}\rangle$	9.847	9.423	10.304	0.000	9.858	0.763	10.125	9.801	10.531	0.000	10.153	0.634
$ 1_{J=0}\rangle$	9.899	9.454	10.364	0.000	9.906	0.788	10.183	9.836	10.595	0.000	10.204	0.658
$ 2_{J=0}\rangle$	9.950	9.486	10.424	0.000	9.953	0.812	10.239	9.871	10.659	0.000	10.256	0.683
$ 3_{J=0}\rangle$	10.045	9.510	10.638	0.000	10.064	0.977	10.338	9.900	10.886	0.000	10.375	0.856
$ 4_{J=0}\rangle$	10.067	9.503	10.587	0.000	10.052	0.939	10.358	9.891	10.832	0.000	10.360	0.815
$ 5_{J=0}\rangle$	10.000	9.519	10.483	0.000	10.001	0.835	10.295	9.906	10.722	0.000	10.308	0.707
HDO												
$ 0_{J=0}\rangle$	9.890	9.442	10.369	0.033	9.900	0.805	10.171	9.823	10.600	0.036	10.198	0.678
$ 1_{J=0}\rangle$	9.953	9.480	10.441	0.039	9.958	0.835	10.241	9.864	10.677	0.042	10.261	0.708
$ 2_{J=0}\rangle$	10.090	9.526	10.678	-0.119	10.098	1.019	10.385	9.917	10.928	-0.129	10.410	0.904
$ 3_{J=0}\rangle$	10.021	9.520	10.518	0.034	10.019	0.867	10.316	9.908	10.759	0.037	10.327	0.740
$ 4_{J=0}\rangle$	10.183	9.557	10.802	0.262	10.180	1.169	10.484	9.953	11.060	0.283	10.499	1.077
$ 5_{J=0}\rangle$	10.110	9.561	10.683	-0.036	10.118	0.974	10.411	9.954	10.933	-0.039	10.433	0.852

take account contributions from the dipole-allowed transitions at infrared and longer wavelengths.⁵⁷ The contribution of these neglected transitions is expected to be significant at $\lambda > 900$ nm. Thus, it is arguable to distrust on the error margins of the experimental estimation $\bar{\alpha}=9.83\pm0.02$ by Russell and Spackman.⁵² An example that would support this affirmation is the $\langle 0_{J=0}|\bar{\alpha}|0_{J=0}\rangle=9.86$ value at the MCSCF (CAS1)/P3 level of theory reported by Luo *et al.*,⁵⁶ close to this experimental estimation. MCSCF (CAS1) is a lower order electron correlation model than CCSD. At the contrary, their $|0_{J=0}\rangle$ vibrational wave function⁵⁶ is almost identical to that presented in Eq. (12) and both P3 and W₆ basis sets have a similar quality somehow.¹⁸ As conclusion, this good agreement would point that the error margins for the experimental estimation of $\bar{\alpha}$ should be larger than those published by Russell and Spackman.⁵²

TABLE X. Comparison of the vibrational average of the static dipole polarizability for the ground vibrational state $|0_{J=0}\rangle$ of H₂O molecule.

	$\langle\alpha_{xx}\rangle$	$\langle\alpha_{yy}\rangle$	$\langle\alpha_{zz}\rangle$	$\langle\bar{\alpha}\rangle$	$\langle\Delta\alpha\rangle$
CCSD/W ₆ ^a	9.93	9.46	10.43	9.94	0.84
MCSCF/ANO ^b	9.52	9.05	10.09	9.55	0.91
MP2/POL1 ^c	10.06	9.71	10.48	10.08	0.66
SE-MRC ^d	9.72	9.30	10.29	9.77	0.86

^aThis work, linear response calculation.

^bRudd, Åstrand, and Taylor (Ref. 53).

^cRussell and Spackman (Ref. 52).

^dSpelsberg and Meyer (Ref. 35).

V. CONCLUSIONS

We have presented static and dynamic at 514.5 nm *ab initio* linear response dipole polarizability surfaces of water using the CCSD model with a basis set of near-Hartree–Fock quality. The $\alpha(514.5$ nm) surface reproduced satisfactorily all the experimental data of the molecular polarizability of the water molecule available to date, though it could be due to a cancellation of electron correlation and basis set truncation errors, as was discussed in Sec. III A. From the simulations of the rotation-vibration Raman spectra, we have confirmed that basis set quality is a decisive factor to calculate accurate *ab initio* dipole polarizability surfaces with an acceptable computational expense. A detailed analysis of the vibrational averages has been also carried out. This work shows that the corrections due to the harmonic and anhar-

TABLE XI. Comparison of the ZPVCs to the mean and anisotropy of the static dipole polarizability for the ground vibrational state $|0_{J=0}\rangle$ of H₂O, D₂O, and HDO molecules.

		CCSD/W ₆ ^a	CPHF/POL1 ^b
H ₂ O	$\langle\bar{\alpha}\rangle^{\text{ZPVC}}$	0.308	0.247
	$\langle\Delta\alpha\rangle^{\text{ZPVC}}$	0.283	0.268
D ₂ O	$\langle\bar{\alpha}\rangle^{\text{ZPVC}}$	0.224	0.180
	$\langle\Delta\alpha\rangle^{\text{ZPVC}}$	0.203	0.195
HDO	$\langle\bar{\alpha}\rangle^{\text{ZPVC}}$	0.266	0.214
	$\langle\Delta\alpha\rangle^{\text{ZPVC}}$	0.245	0.231

^aThis work, linear response calculation.

^bLuis *et al.* (Ref. 54).

monic contributions of the wave functions to the vibrational averages of the dipole polarizability are of the same order in H₂O, D₂O, and HDO molecules. Higher quality dipole polarizability surfaces might, in principle, be obtained using, for instance, the CC3 iterative approximate coupled-cluster single, doubles, and triples model⁵⁸ with more complete basis sets than W₆ [for instance, PA (Ref. 19) and PA1], although the computational effort would be very expensive for the time being.

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- ¹A. Mosyak, P. Graf, I. Benjamin, and A. Nitzan, *J. Phys. Chem. A* **101**, 429 (1997); I. Benjamin, D. Evans, and A. Nitzan, *J. Chem. Phys.* **106**, 6647 (1997).
- ²B. D. Bursulaya and H. J. Kim, *J. Chem. Phys.* **109**, 4911 (1998); **110**, 9656 (1999).
- ³S. Yoo, A. Ley, and X. C. Zeng, *J. Chem. Phys.* **119**, 6083 (2003).
- ⁴G. Lamoureux, A. D. MacKerell, and B. Roux, *J. Chem. Phys.* **119**, 5185 (2003).
- ⁵C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1984), Vol. 1.
- ⁶A. Morita, *J. Comput. Chem.* **23**, 1466 (2002).
- ⁷A. Amadei, M. Aschi, R. Spezia, and A. Di Nola, *J. Mol. Liq.* **101**, 181 (2002).
- ⁸R. Chelli, R. Righini, S. Califano, and P. Procacci, *J. Mol. Liq.* **96**, 87 (2002).
- ⁹N. Bloembergen, *Non Linear Optics* (Benjamin, New York, 1965).
- ¹⁰M. J. Smit, G. C. Groenenboom, P. E. S. Wormer, A. van der Avoird, R. Bukowski, and K. Szalewicz, *J. Phys. Chem. A* **105**, 6212 (2001).
- ¹¹P. W. Fowler, *Theory and Calculation of Molecular Properties*, Annual Report C Vol. 84 (Royal Society of Chemistry, London, 1987), p. 3; A. A. Hasanein, *Adv. Chem. Phys.* **85**, 415 (1993); A. Hinchliffe, *Ab Initio Determination of the Structures and Properties of Molecules* (Elsevier, Amsterdam, 1988); D. M. Bishop, *Adv. Quantum Chem.* **25**, 1 (1994); J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (Word Scientific, London, 1995), p. 857; Y. Luo, H. Ågren, P. Jørgensen, and K. V. Mikkelsen, *Adv. Quantum Chem.* **26**, 165 (1995); M. Nakano and K. Yamaguchi, in *Trends in Chemical Physics* (Research Trends, Trivandrum, 1997), Vol. 5; D. Pugh, in *Chemical Modelling: Applications and Theory*, edited by A. Hinchliffe (The Royal Society of Chemistry, London, 2000), Vol. 1; D. M. Bishop and P. Norman, in *Handbook of Advanced Electronic and Photonic Materials*, edited by H. S. Nalwa (Academic, San Diego, 2000); B. Champagne and B. Kirtman, in *Handbook of Advanced Electronic and Photonic Materials*, edited by H. S. Nalwa (Academic, San Diego, 2000).
- ¹²D. M. Bishop, *Rev. Mod. Phys.* **62**, 343 (1990).
- ¹³D. M. Bishop, B. Kirtman, H. A. Kurtz, and J. E. Rice, *J. Chem. Phys.* **98**, 8024 (1993); B. Kirtman and B. Champagne, *Int. Rev. Phys. Chem.* **16**, 389 (1997); D. M. Bishop, *Adv. Chem. Phys.* **104**, 1 (1998).
- ¹⁴G. Avila, G. Tejeda, J. M. Fernández, and S. Montero, *J. Mol. Spectrosc.* **220**, 259 (2003).
- ¹⁵G. Avila, G. Tejeda, J. M. Fernández, and S. Montero, *J. Mol. Spectrosc.* **223**, 166 (2004).
- ¹⁶G. Avila, J. M. Fernández, G. Tejeda, and S. Montero, *J. Mol. Spectrosc.* **228**, 38 (2004).
- ¹⁷E. R. Davidson and D. Feller, *Chem. Rev. (Washington, D.C.)* **86**, 681 (1986); I. Shavitt, *Isr. J. Chem.* **33**, 357 (1993).
- ¹⁸G. Maroulis, *J. Chem. Phys.* **94**, 1182 (1991).
- ¹⁹G. Maroulis, *Chem. Phys. Lett.* **289**, 403 (1998).
- ²⁰K. Pierloot, B. Dumez, P. O. Widmark, and B. O. Roos, *Theor. Chim. Acta* **90**, 87 (1995).
- ²¹P. O. Widmark, P. A. Malmqvist, and B. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- ²²P. O. Widmark, B. J. Persson, and B. Roos, *Theor. Chim. Acta* **79**, 419 (1991).
- ²³<http://www.teokem.lu.se/molcas/downloads.html>
- ²⁴A. Szabvo and N. S. Ostlund, *Modern Quantum Chemistry* (MacMillan, New York, 1982).
- ²⁵S. Wilson, *Electron Correlation in Molecules* (Clarendon, Oxford, 1984).
- ²⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN98, Revision A.11.3, Gaussian, Inc., Pittsburgh PA, 2002.
- ²⁷T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*, DALTON, a molecular electronic structure program, Release 1.2 (2001).
- ²⁸G. Maroulis, *J. Chem. Phys.* **108**, 5432 (1998).
- ²⁹G. Maroulis, *Chem. Phys. Lett.* **177**, 352 (1991).
- ³⁰O. Christiansen, A. Halkier, H. Koch, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **108**, 2801 (1998).
- ³¹I^r representation, customarily used for prolate top molecules; P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy* (NRC Research Press, Ottawa, 1998).
- ³²A. J. Stone, *The Theory of Intermolecular Forces* (Clarendon, Oxford, 1995).
- ³³G. Avila, J. M. Fernández, B. Maté, G. Tejeda, and S. Montero, *J. Mol. Spectrosc.* **196**, 77 (1999).
- ³⁴T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, and R. J. Harrison, *ibid.* **96**, 6769 (1992).
- ³⁵D. Spelsberg and W. Meyer, *J. Chem. Phys.* **108**, 1532 (1998).
- ³⁶A. J. Sadlej, *Theor. Chim. Acta* **79**, 123 (1991).
- ³⁷J. Almlöf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).
- ³⁸Based on the Full-CI correlation correction obtained from the aug-cc-pVDZ basis set (+0.75) and an estimation of the SCF/CBS value (8.54); D. Feller, *J. Chem. Phys.* **98**, 7059 (1993).
- ³⁹G. Maroulis, *J. Chem. Phys.* **118**, 2673 (2003).
- ⁴⁰G. Maroulis, *Chem. Phys. Lett.* **291**, 81 (2003).
- ⁴¹J. K. G. Watson, *Mol. Phys.* **15**, 479 (1968).
- ⁴²R. Lanquettin, L. H. Coudert, and C. Camy-Peyret, *J. Mol. Spectrosc.* **206**, 83 (2001).
- ⁴³H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997).
- ⁴⁴A. H. Harvey, J. S. Gallagher, and J. M. H. Levelt Sengers, *J. Phys. Chem. Ref. Data* **27**, 761 (1998).
- ⁴⁵W. F. Murphy, *J. Chem. Phys.* **67**, 5877 (1977).
- ⁴⁶J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, and P. F. Bernath, *J. Phys. Chem. Ref. Data* **30**, 735 (2001).
- ⁴⁷I. G. John, G. B. Backsay, and N. S. Hush, *Chem. Phys.* **38**, 319 (1979).
- ⁴⁸A. Stirling, *J. Chem. Phys.* **104**, 1254 (1996).
- ⁴⁹S. A. Perera and R. J. Barlett, *Chem. Phys. Lett.* **314**, 381 (1999).
- ⁵⁰W. F. Murphy, *Mol. Phys.* **33**, 1701 (1977).
- ⁵¹W. F. Murphy, *Mol. Phys.* **36**, 727 (1978).
- ⁵²A. J. Russell and M. A. Spackman, *Mol. Phys.* **84**, 1239 (1995).
- ⁵³K. Ruud, P.-O. Åstrand, and P. R. Taylor, *J. Chem. Phys.* **112**, 2668 (2000).
- ⁵⁴J. M. Luis, M. Duran, J. L. Andrés, B. Champagne, and B. Kirtman, *J. Chem. Phys.* **111**, 875 (1999).
- ⁵⁵O. Quinet, D. Champagne, and B. Kirtman, *J. Comput. Chem.* **22**, 1920 (2001).
- ⁵⁶Y. Luo, H. Ågren, O. Vahrtras, P. Jørgensen, V. Spirko, and H. Hettema, *J. Chem. Phys.* **98**, 7159 (1993).
- ⁵⁷G. D. Zeiss and W. J. Meath, *Mol. Phys.* **30**, 161 (1975).
- ⁵⁸K. Hald, P. Pawłowski, P. Jørgensen, and C. Hättig, *J. Chem. Phys.* **118**, 1292 (2003).