Role of Cancellation of Errors in Ab Initio Calculations: Structure and Energetics of the OH^- (H_2O) System and Electric Dipole Properties of the Subsystems

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The joint study of the full system and of the electric dipole properties of the subsystems allows an analysis of the role of cancellation of errors on the geometry and energetics of $OH^-(H_2O)$. Calculations were performed at the Hartree−Fock, MP*n* ($n = 2-4$) and CCSD(T) levels. The ab initio dipole moment and static dipole polarizability of OH^- and H_2O were computed using 15 or so basis sets. Special attention was paid to the delicate case of the polarizability of OH^-, which requires much more diffuse polarization functions than for H_2O. The MP*n* series does not converge to the CCSD(T) values. Our recommended values for the parallel and perpendicular polarizability components of OH^- are 27.8 and 46.7 au, respectively. For several basis sets, the geometry of the $OH^-(H_2O)$ system was optimized, accounting or not for the basis set superposition error (BSSE) in the optimization process. Energetic and geometric data are discussed. From our best calculations, ΔH (298 K) lies around 26.4−26.7 kcal mol^{-1}, in excellent agreement with the most recent experimental values of -26.5 ± 1.0 (Meot-Ner, M.; Speller, C. V. *J. Phys. Chem.* **1986**, *90*, 6616). Some bases underestimate the polarizability components of OH^-, the effect on the intermolecular energetic contributions being counterbalanced by the BSSE. However, such an "advantageous" balance cannot be guessed "a priori".

I. Introduction

The hydroxide anion is quite commonly found in nature. It is encountered in the gas phase (in particular in the atmosphere) or in the liquid and condensed phases. Given the importance of water in our world, it is not surprising that this anion, common in fields such as biology, physics, or chemistry, is often in the hydrated form. Although less studied than their protonic counterparts, these hydrates have been the subject of many theoretical publications. We reported in a recent paper[1] that seven publications appeared in the 70s, 28 in the 80s, 26 in the 90s, and six in the early 2000s. Among them, many are quantum mechanical studies and in particular ab initio calculations. The first attempts were based on Hartree−Fock (HF) calculations with small basis sets and crude geometrical optimizations.[2] The accuracy of the studies then followed the evolution of the theory and the progress of the computer facilities. The hydroxide anion monohydrate was thus treated at the correlated level, according to the methods available, and somewhat larger basis sets were used.[3−13] A qualitative change arose around 1995, following the evolution of the computer resources. The need for diffuse functions (and in particular diffuse polarization functions) to correctly describe the intermolecular interactions in ab initio calculations became better acknowledged after this date. Although this need was known for several decades, the computer limitations did not allow the use of extended basis sets at the correlated level, except for very small systems. The work published since 1995 is generally based on the use of much larger polarized and diffuse basis sets than in the previous periods.[14−24] The need for such a large basis set holds for density functional theory (DFT) calculations too, which became popular at this time.[13,17,19,21,25]

The problem of the basis sets underlies in fact two kinds of difficulties encountered in the treatment of the intermolecular

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interactions: the correct description of the molecular electric properties and the basis set superposition error (BSSE) in the supermolecule treatment. Both questions, although related, are however partly disconnected. Let us consider them separately.

Among the molecular electric properties, the role of diffuse polarization functions to describe the molecular polarizability is crucial. Indeed, this was already shown 30 years ago for the dispersion energy,[26] which is closely related to the molecular polarizability of the subsystems. This was rationalized some years later for ab initio calculations of the polarizabiblity.[27] Many accurate calculations have been published on the water polarizability, especially since the 80s.[28−46] These papers generally report the role of both the basis sets and the correlation contribution, computed with various methods. Polarization functions are commonly added to the usual atomic basis sets used in molecular calculations. This generated a few categories of diffuse polarized basis sets, which will be discussed in the Computational Details section. The polarizability of the hydroxide anion did not receive as much attention as that of water. Indeed, only a few accurate papers appeared, between 1986 and 1992.[47−51] We could believe that the problem of the correct description of the polarizability of OH^- was definitely solved because of the quality of the papers cited above. However, it seems that it is just purely ignored in many of the studies that appeared on the hydroxide anion hydrates, even for the monohydrate. Quite often, the basis sets selected to treat the $OH^-(H_2O)$ heterodimer are adequate for the description of the water polarizability but maybe not for OH^-. It is thus highly relevant to examine the adequacy of some of the most widely used bases in this field.

The choice of a proper basis set is not only crucial to describe the molecular properties that play an important role in intermolecular interactions, such as the molecular polarizability. Another delicate problem is the BSSE due to the possibility, in the heterodimer, that each molecule can take advantage of the basis set of the other molecule to artificially improve its own energy. This point was discussed for the hydroxide anion monohydrate at various levels of the theory and with different basis sets: HF and MP2 levels for the 6-311++G(d,p) basis[16] and the 6-31++G(d) basis;[22] MP2, MP4, and CCSD(T) levels for the aug-cc-pVxZ series;[23] MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels for both the 6-311++ series augmented with (nd, np, $n = 1-3$) or (3df, 3pd) functions and the aug-cc-pVxZ series.[24] In all cases, the BSSE was corrected using the Boys and Bernardi procedure.[52] This correction is widely used to correct the interaction energy. However, it is generally not included at the geometry optimization level. As shown for other systems, both the geometry and the energy should be corrected.[53] In particular, the BSSE leads to too short intermolecular distances. A corrected interaction energy computed for an uncorrected geometry may thus be inaccurate. A small BSSE associated with large polarized and diffuse bases gives the guarantee of a correct intermolecular geometry. However, fulfilling both of these conditions may not be easy. A small BSSE does not guarantee that the intermolecular interaction between the subsystems is correctly described, and on the other hand, the basis sets including diffuse functions to describe it often lead to a large BSSE. The automation of the geometric optimization on BSSE-corrected potential surface, as recently proposed,[54] now allows a more refined analysis of this question.

An inspection of the literature concerning the $OH^-(H_2O)$ system shows a rather paradoxical feature; studies on the interaction energy and on the polarizability components of the subsystems are generally disconnected. Basis sets of variable accuracy are used to describe the full system. Information on the efficiency of such bases to describe the polarizability is available for water but not for the hydroxide anion. Although extrapolation procedures should allow an improved accuracy in the prediction of energies and molecular properties (see ref 55 for a comparison between several extrapolation procedures), we found that such a correction was applied to the energy contribution but not generalized to estimate the complete basis set (CBS) limit of the molecular polarizability. Furthermore, the most accurate calculations of the $OH^-(H_2O)$ system neglect the effect of the BSSE correction on the optimized geometry. For these reasons, we undertook a detailed examination of these two sources of inaccuracy: description of the electric properties of the subsystems and effect of the BSSE correction on the geometry of the full system.

The present paper gathers our main results, using several series of basis sets commonly used in the intermolecular interactions field. Concerning the electric properties of the subsystems, we will show that the most delicate problem is the description of the static dipole polarizability tensor components of OH^-. For some significant basis sets, we will then examine the effect of the BSSE correction on the geometries (and consequently the energetics) of the full system. The paper will be organized as follows: the methods used, the computational details on the basis sets, and the geometries will be briefly described in Section II. The results will be presented and discussed in Section III. Finally, we will conclude in Section IV.

II. Methods of Calculation and Computational Details

A. Methods of Calculation. Calculations were performed at the HF, MP2, MP3, MP4, and CCSD(T) levels, using the Gaussian 98 package.[56] The polarizability tensor components were obtained using either analytic expressions when available (HF and MP2 wave functions) or the finite field method in the general case.[57−60] In the last case, the polarizability components were obtained as the numerical second derivative of the energy according to the following expression:[58,60]

$$\alpha_{ii} = \frac{\{2E(0) - E(F_i) - E(-F_i)\}}{F_i^{\,2}} + O(F_i^{\,2}), \quad i = x, y, \text{ or } z \tag{1}$$

where $E(F_i)$ is the energy of the system computed in the electric field of strength F_i. We discussed in a recent paper[61] the accuracy that can be reached from this parabolic fit. More accurate results are obtained with a quartic polynomials fit. These points will be commented on in Section III.

The $OH^-(H_2O)$ system studies were based on the supermolecule approach. For two closed shell molecules A and B, the interaction energy is given by the standard formula

$$E_{\text{int}}^{\text{SM}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \tag{2}$$

where the superscript SM refers to the supermolecule system. In this paper, the general superscript SM will be replaced by the level of the calculation, that is, HF for the HF calculations, MPn for the Møller−Plesset perturbation theory calculations through the order n, and CCSD(T) for the coupled cluster single and double excitation calculations with an approximate inclusion of the connected triple excitations.[62−65] The supermolecule interaction energies were corrected for the BSSE using the counterpoise correction of Boys and Bernardi,[52] which implies that the wave function of each monomer is computed using the

TABLE 1: Basis Sets: Exponent of the Most Diffuse Function

N[a]	basis	s (O/H)	p (O/H)	d (O/H)	f (O/H)	g (O/H)
33	S	.090030/0.032400	.0638500/0.0324000	.06390/		
39	S+	.002416/0.032400	.0189747/0.0324000	.06390/		
47	S++	.002416/0.032400	.0056370/0.0324000	.01900/		
51	S++,+	.002416/0.010220	.0056370/0.0102216	.01900/		
63	S++1f,+1d	.002416/0.010220	.0056370/0.0102216	.01900/0.24700	.500/	
75	S++2f,+2d	.002416/0.010220	.0056370/0.0102216	.01900/0.10000	.200/	
87	R-ANO	.002876/0.027962	.0055260/0.0988270	.05526/0.29104	.376/	
19	cc-pVDZ	.302300/0.122000	.2753000/0.7270000	1.18500/		
44	cc-pVTZ	.238400/0.102700	.2140000/0.3880000	.64500/1.05700	1.428/	
32	aug-cc-pVDZ	.078960/0.029740	.0685600/0.1410000	.33200/		
69	aug-cc-pVTZ	.073760/0.025260	.0597400/0.1020000	.21400/0.24700	.500/	
126	aug-cc-pVQZ	.069590/0.023630	.0534800/0.0848000	.15400/0.19000	.324/0.36	.714/
45	d-aug-cc-pVDZ	.020624/0.007250	.0170740/0.0273466	.09302/		
94	d-aug-cc-pVTZ	.022821/0.006213	.0166769/0.0268144	.07100/0.05772	.175/	
21	6-311++G	.084500/0.036000	.0845000/-			
29	6-311++G**	.084500/0.036000	.0845000/0.7500000	1.29200/		

[a] Number of basis functions for OH$^-$, considering 5d and 7f components.

atomic basis set of the full system. The BSSE is thus given by

$$\mathrm{BSSE} = E_{\mathrm{A}}(\mathrm{ab}) - E_{\mathrm{A}}(\mathrm{a}) + E_{\mathrm{B}}(\mathrm{ab}) - E_{\mathrm{B}}(\mathrm{b}) \tag{3}$$

where (ab), (a), and (b) refer to the use of the basis sets of the full system AB, of the monomer A, or of the monomer B, respectively, to compute the energy of each monomer.

The gradient technique implemented in the Gaussian 98 package was used for the geometry optimization. For some significant cases, the counterpoise correction was taken into account in the geometry optimization process, according to the method proposed by Simon et al.,[54] using their Gaussian links driver.[66]

B. Basis Sets. A total of 18 basis sets were generated from four series of basis sets commonly used in this field. The 18 sets were built by extending the initial sets with additional polarization and diffuse functions. Because of its crucial role, the exponent of the most diffuse function on O and H is reported for all bases and each symmetry in Table 1. Because the adequacy of the basis sets is especially delicate for the description of the hydroxide anion polarizability, we also report the number of contracted functions on OH$^-$. The four series of basis sets are the following:

(i) The R-ANO basis set is built from an ANO basis set (denoted by (14.9.4.3)[6.5.3.2] for O and (8.4.3)[4.3.2] for H[67] according to the (GTO)[CGTO] standard notation) extended with three diffuse s, two diffuse p, and one diffuse d type functions on the oxygen atom. These diffuse functions, obtained from the ratio of the last two consecutive functions of each type, ensure a correct description of the electric properties of the first Rydberg excited states of water.[30] This leads to 9.7.4.2 contracted functions on O and 4.3.2 contracted functions on H, which we will denote by [9.7.4.2/4.3.2]. The R-ANO basis set was successfully used to describe the electric properties of the first excited states of the water molecule.[30,35]

(ii) The polarized medium size (GTO)[CGTO] basis, referred to as basis S in the present paper (often referred to as "Pol1" in the literature), is sequential, with [5.3.2/3.2] contracted functions on O and H, respectively. This relatively small basis in this field was proposed by Sadlej and gives good performance in calculations of electric properties of molecules in their ground state.[29] Some years ago, we extended this basis with three s and one p type diffuse functions on the oxygen atom to study the electric properties of the first excited states of $H_5O_2^+$ at the CASPT2 level.[36] It was denoted by S+ in our initial paper[36] with (13.7.4/6.4)[8.4.2/3.2] functions. The diffuse exponents were obtained in the same way as for the R-ANO basis. In the present work, more diffuse and polarization functions were added, generating bases denoted by S++; S++,+; S++1f,+1d; S++2f,+2d; S++f′1f,+d′1d; and S++f′2f,+d′2d. Basis S++ was deduced from basis S by the addition of three diffuse s, two diffuse p, and one diffuse d type functions on the oxygen atom. Basis S++,+ was deduced from S++ by the addition of one diffuse s and one diffuse p type functions on the hydrogen atom. Bases S++1f,+1d and S++2f,+2d were deduced from basis S++,+ by the addition of one or two diffuse f type functions on the oxygen and d type functions on the hydrogen atoms. To avoid unbalanced bases, a nondiffuse polarization function of type f or d (denoted hereafter by f′ and d′) was also added to the last two bases, leading to bases S++f′1f,+d′1d and S++f′2f,+d′2d.

(iii) The third category of bases corresponds to the cc-pVXZ, aug-cc-pVXZ, and x-aug-cc-pVXZ series proposed by Dunning et al. The polarized cc-pVXZ bases were derived to account for the correlation effects.[68] They were extended with some diffuse functions in order to properly describe electron affinities.[69] A few studies of atomic and molecular polarizability[37,41,70,71] use the x-aug-cc-pVXZ series proposed by Dunning et al.[72] In this series, more diffuse functions are added to improve the description of electric properties. Comparisons of aug-cc-pVXZ and x-aug-cc-pVXZ bases are scarce. While the improvement due to the x-aug-cc-pVXZ is small for diatomic radicals,[71] it can be quite important for anions.[72] The d-aug-cc-pVDZ and d-aug-cc-pVTZ bases were thus considered here.

(iv) The last category of bases is illustrated by the 6-311++G and 6-311++G** sets.[73] These bases are often used in the literature to treat dimers (or heterodimers) of molecules (see ref 74 and references therein), in particular for the OH$^-$(H_2O) system.[16,24]

C. Geometries. The experimental geometry was used in the calculations of the polarizability and dipole moment components of the monomers (r(OH) = 0.9572 Å and ∠HOH = 104.5° for the water molecule,[75] r(OH$^-$) = 0.964 Å for the hydroxide ion[76]). The water molecule was in the *yz* plane, with the C_{2v}-axis along the *z*-axis. OH$^-$ was along the *z*-axis.

A full optimization of the geometric parameters of the OH$^-$(H_2O) system was performed at the MP2 level with the basis sets of the S and of the aug-cc-pVXZ series. The geometries were optimized either on the uncorrected or on the BSSE-corrected hypersurfaces.

III. Numerical Results and Discussion

In this section, we will first examine the static polarizability and the dipole moments of the subsystems, which play a dominant role in the intermolecular interactions. This will be followed by the study of the $OH^-(H_2O)$ monohydrate.

A. Polarizability Components. The accuracy of the polarizability components from ab initio calculations depends on three main factors: the adequacy of the basis set, the effect of the electron correlation calculation level, and the method used to obtain the polarizability components (analytical or numerical). These three points are closely interconnected.

The last point was examined in detail in a recent study of the OH^- anion,[61] using analytical expressions or the finite field method at the MP2 and CCSD(T) levels. Before analyzing the other two points, it is relevant to recall the main features obtained in that study. They will be reported in Section III.A.1.

The first point, namely, the effect of the basis set on the polarizability components, will be discussed in details in the present paper. As written in the Introduction (Section I), the choice of an adequate basis set for the OH^- anion is more delicate than for the neutral water; in particular, more diffuse functions are needed. In the systematic comparison of the polarizability components obtained with the 18 basis sets selected, a special attention was thus paid to the OH^- anion (Section III.A.2).

The second point will be illustrated by calculations at the HF, MP2, MP3, MP4, and CCSD(T) levels. These methods will be compared, and the convergence of the MP*n* series will especially be examined (Section III.A.3).

1. Accuracy of the Analytic and Finite Field Calculations. The analysis given in our previous study[61] was based on MP2 and CCSD(T) calculations, using basis S+. It is representative of the general problems of accuracy encountered with other levels of the wave function. The main features are thus gathered here.

MP2 Calculations. The MP2 analytical calculations of the static polarizability components of OH^- were quite stable for an SCF convergence threshold varying from 10^{-7} to 10^{-12} au. The use of the finite field method was more delicate. With a parabolic fit, the results were dependent on both the field strength and the convergence of the wave function. For a field strength of 0.001 au, the error on the α_{xx} component was 0.02, 0.02, and 0.03 au for the convergence threshold of 10^{-12}, 10^{-10}, and 10^{-7} au, respectively (the analytic value being 36.149 au with basis S+). An optimized field strength of 0.0002 au lead to an excellent agreement with the analytical results with a tight convergence, but the error reached 0.2 au with a convergence threshold of 10^{-7} au. We must mention that the “unconverged” decimals were retained in all of these calculations, whatever the convergence threshold, as done in general purpose quantum chemistry codes. The error would be much larger if only the converged decimals were retained (see the discussion on this point in our previous paper[61]).

A quartic polynomials fit with a tight convergence lead to an excellent agreement with the analytic values, rather independent of the field strengths used; the values obtained with the field strengths of either 0.001 and 0.0002 au or 0.001 and 0.002 au were nearly identical (and nearly identical to the analytic ones).

The error due to the higher order terms of the polarizability in the multipole expansion was also analyzed. It becomes predominant with large field strengths. In the parabolic fit, the leading term to this contribution depends on the γ components. In the quartic polynomials fit, this leading term vanishes, the new one arising from the next higher order term. Accurate results can then be obtained from the finite field method associated with a quartic polynomials fit and a tight convergence.

CCSD(T) Results. A high accuracy was less easily obtained with CCSD(T) calculations, mainly due to problems of convergence of the CCSD wave function. A convergence threshold of only 10^{-9} au could be reached on the CCSD energies. No analytical expressions were available to compute the static polarizability components at the CCSD(T) level. Extrapolating the analysis done on the MP2 calculations, we considered that the finite field method associated with the quartic polynomials fit and the convergence threshold of 10^{-9} au was able to give accurate results, taken as reference values.

With the convergence threshold of 10^{-9} au, the error on the α_{xx} component given by the parabolic fit was 0.17, 0.04, and 0.002 au for the field strength of 0.002, 0.001, and 0.0002 au, respectively (the quartic polynomials fit value being 40.2213 au, using the field strengths of 0.002 and 0.001 au). With the convergence threshold of 10^{-7} au, the error became 0.17, 0.1, and 1.3 au, respectively. Clearly, such a threshold is not recommended with the small field strength of 0.0002 au. The error given by a quartic polynomials fit (field strength of 0.002 and 0.001 au) associated with the convergence threshold of 10^{-7} au was only 0.05 au.

As long as we limit our analysis to the qualitative behavior obtained with various categories of basis sets and methods, the convergence threshold (10^{-7} au) associated with a parabolic fit and a field strength of 0.001 au was retained. The largest error found in the previous analysis (0.1 au) gives an estimate of the order of magnitude of the error involved, which may be somewhat dependent on the basis set. For more accuracy, a better convergence and a quartic polynomials fit have to be employed.

2. Effect of the Electron Correlation Calculation Level. Before comparing various methods, the convergence of the Møller−Plesset expansion deserves special attention. We already discussed this important point in the case of the two-body[1] and three-body[77] intermolecular interaction energies. In both cases, an oscillating pattern and a probable divergence of the series were found for some structures. It is thus relevant to examine the situation in the case of the polarizability. For this sake, the polarizability components of the OH^- anion obtained with some basis sets are collected in Table 2. They are representative of the general case.

Table 2 clearly shows an oscillating pattern of the MP*n* series. The MP2 results lie in the same range as the CCSD(T) ones for the $\alpha_{\parallel}$ ($= \alpha_{zz}$) component and are somewhat smaller for the $\alpha_{\perp}$ ($= \alpha_{xx} = \alpha_{yy}$) one (by about 10% in the S series). The MP3 values are systematically smaller than the MP2 ones, while the MP4 results are significantly larger than all of the others and in particular than the CCSD(T) ones. Within the MP4 order, the contributions regularly increase when accounting for the SQ, SDQ, or the total MP4 terms. The MP4(SDQ) values are in the range of the CCSD(T) ones. It is not possible to extrapolate from these results if the MP*n* series will either converge to values different of the CCSD(T) ones or will diverge. Considering the opposite sign of the MP3 and MP4 correlation contributions also found in their own work, Pluta et al.[48] suggested that the fifth-order correction may again occur with altered sign, canceling some of the fourth-order contribution. Given these uncertainties, the MP3 and MP4 levels will not be considered in the rest of this work.

The values of the polarizability components of OH^- are plotted in Figure 1 for all bases and at various levels of the electron correlation calculation. The electron correlation effect

TABLE 2: Convergence of the Parallel and Perpendicular Components of the OH^- Polarizability with the Size of the Basis Set and the Level of the Theory; Values in au

	S+	*S*++	*S*++, +	*S*++1*f*, +1*d*	*S*++2*f*, +2*d*	R-ANO	d-aug-cc-pVTZ
				$\alpha_{\parallel}$			
HF	17.04	18.50	18.50	18.60	18.67	18.40	18.54
MP2	21.71	27.03	26.87	26.99	27.27	25.17	26.17
MP3	18.92	21.06	21.07	21.06	21.07	20.28	20.55
MP4(DQ)	19.90	23.33	23.26	23.23	23.35	21.82	22.46
MP4(SDQ)	21.78	28.64	28.36	28.28	28.51	26.61	26.20
MP4	24.00	33.26	32.88	32.91	33.34	28.45	30.73
CCSD(T)	21.59	28.59	28.35	27.96	28.07	24.85	26.38
				$\alpha_{\perp}$			
HF	20.92	22.86	22.83	22.78	23.27	23.30	23.09
MP2	36.15	42.72	42.50	42.11	43.04	40.85	40.49
MP3	26.37	29.11	29.08	28.72	29.37	28.05	27.97
MP4(DQ)	29.91	34.26	34.14	33.61	34.30	32.22	32.14
MP4(SDQ)	38.39	46.78	46.48	45.53	46.28	40.64	40.69
MP4	45.54	56.91	56.49	55.55	56.70	50.47	50.42
CCSD(T)	40.33	48.79	48.53	46.56	47.42	43.16	42.72

is much larger for the $\alpha_{\perp}$ than for the $\alpha_{\parallel}$ component. For all bases, the MP2 and CCSD(T) values of the $\alpha_{\parallel}$ component are close, whereas the CCSD(T) values are somewhat larger than the MP2 ones for the $\alpha_{\perp}$ component with the d-aug-cc-pVXZ, R-ANO, and S series. This confirms that the diffuse functions, included in these three series but missing in the cc-pVXZ one, are more important for the perpendicular than for the parallel component.

A similar comparison is available for the water molecule in Figure 2. Because the α_{xx} and the α_{zz} components are close, only the last one is reported in Figure 2. The CCSD(T) and MP2 results are now quite similar for any component. The effect of the electron correlation is much smaller for the water molecule than for the anion. It does not exceed 10%, while it commonly reaches 20% and even exceeds 50% for the perpendicular component of the anion. As a consequence, we can understand that the description of the water molecule polarizability may be less critical than that of the hydroxide anion. In particular, the need for diffuse functions in the basis sets is less important.

This analysis shows that the effect of the level of the electron correlation calculation may be quite different for the anion and the water molecule. This means that conclusions obtained for the water molecule cannot be extrapolated without care to the anion. This is especially true to get a proper description of the $\alpha_{\perp}$ component of the anion.

3. Efficiency of the Basis Sets. Figures 1 and 2 allow an analysis of the efficiency of the basis sets to describe the polarizability components of the OH^- and water molecules. To make the comparison easier, the basis sets are grouped by categories on the diagrams, polarization and diffuse functions being successively added within each category.

Let us first consider the polarizability components of OH^- (Figure 1). The reference values, obtained with the S++f′2f,+d′2d basis and a quartic polynomials fit at the MP2 and CCSD(T) levels, are 27.14 and 27.81 au, respectively, for the $\alpha_{\parallel}$ component, and 42.73 and 46.58 au, respectively, for the $\alpha_{\perp}$ component. The parabolic fit values reported in Figure 1 (S++f′2f,+d′2d basis) are in agreement with them, within 0.1

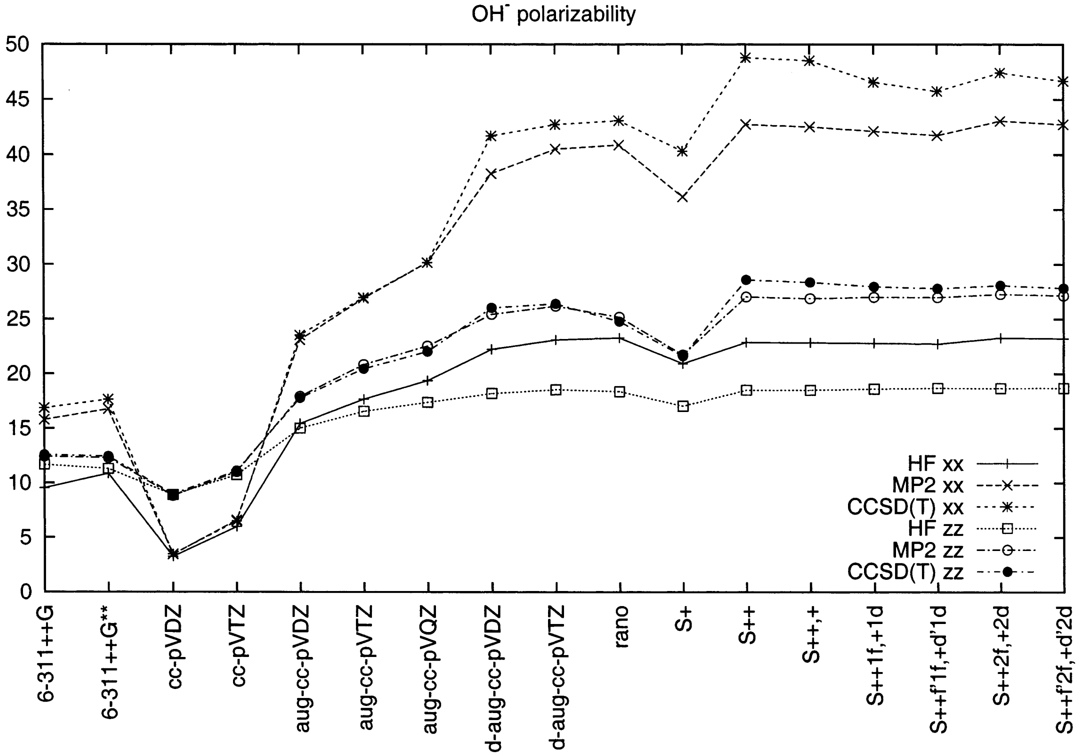

Figure 1. Static dipole polarizability components of OH^- (in au, basis sets given in abscissa).

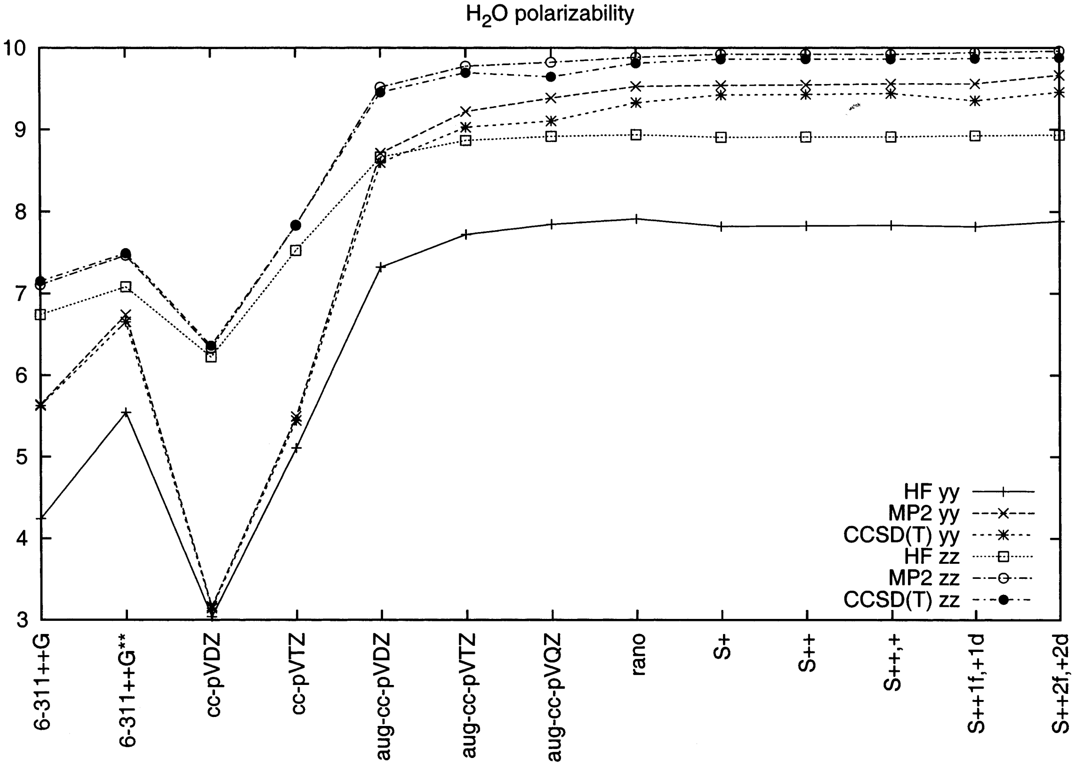

Figure 2. Static dipole polarizability components of H_2O (in au, basis sets given in abscissa).

au in the worst case according to the error discussed in Section III.A.1. If we except the S+ basis, which obviously misses some contributions, the diagram can be divided into two parts. The limit is approximately given by the aug-cc-pVQZ basis. The bases reported on the left side strongly underestimate both components, even at the HF level. It is clear that the bases, which do not include some dedicated diffuse (valence and polarization) functions, cannot properly describe the polarizability components, in particular the $\alpha_\perp$ one. This is the case of the aug-cc-pVXZ series (X = D, T, Q), a qualitative change occurring with the d-aug-cc-pVDZ basis. It is consistent with the exponents reported in Table 1. The last p(O) and d(O) exponents play a dominant role (compare for instance bases S+ and S++). The higher symmetry functions have only a minor role, improving the quality of the results but involving no qualitative change. This suggests that the small improvement seen in Figure 1 when going from the aug-cc-pVDZ to the aug-cc-pVQZ bases or from the d-aug-cc-pVDZ to the d-aug-cc-pVTZ bases may be due to the decrease of the last p(O) and d(O) exponents rather than to the addition of higher symmetry functions. More generally, the d-aug-cc-pVXZ and the R-ANO correlated results are somewhat underestimated (by more than 10% for the d-aug-cc-pVDZ basis) whereas the S++ and S+++ correlated values are overestimated by about 4%. Such an analysis is of great practical interest if we consider the number of basis functions needed for a calculation of the polarizability of OH^-. Consequently, because the huge aug-cc-pVQZ basis requires 126 functions and needs additional ones (leading to a d-aug-cc-pVQZ basis), we did not explore further on this series.

The diagram obtained for the water molecule (Figure 2) is much more homogeneous. We can again divide it into two parts. However, the limit now is rather given by the aug-cc-pVDZ basis. Indeed, the aug-cc-pVDZ values, although slightly underestimated (by about 6%), start the plateau of reliable results. The aug-cc-pVXZ series can be considered as a smooth transition between bases unable or able to give correct results. Also, the S+ basis, which misses some contributions in the case of the hydroxide anion, is suitable for the polarizability of the water molecule. This is especially interesting from a practical point of view since the S+ basis is hardly larger than the aug-cc-pVDZ basis and gives better results. As noted for the anion, the *zz* component (along the C_{2v}-axis), is less sensitive to the basis set than the other components.

These results show that artifacts can be introduced in the treatment of the $OH^-(H_2O)$ system with basis sets that do not correctly describe both subsystems. An analysis of some of the inaccuracies involved is given in Section III.C.

4. Comparison with Previous Calculations of the OH^- Polarizability. The values previously published in the literature[47-51] are collected in Table 3, together with our best results obtained for each series of the basis sets studied in the present work. They correspond to bases d-aug-cc-pVTZ, R-ANO, and S++f′2f,+d′2d. We also included the aug-cc-pVDZ basis, which was used in previous studies of the $OH^-(H_2O)$ system.[1,15,18,77]

We already discussed the results obtained with the aug-cc-pVDZ basis, which does not correctly describe the correlation contribution to both components, more especially the perpendicular one, and underestimates them even at the SCF level. The small basis S (also called Pol1[48]) gives much better results: although somewhat too small, they are not out of the range. The other bases lead to rather similar values. Those given by the [5.3.3/3.3], d-aug-cc-pVTZ, and R-ANO bases are close, slightly smaller than those given by the EFV (electric field variant) and S++f′2f,+d′2d ones. Although it is very delicate to definitely conclude, the CCSD(T) values obtained with the S++f′2f,+d′2d basis (27.8 and 46.7 au) are probably close to the true ones.

B. Dipole Moments. Because the dipole moments play a crucial role in the interaction between OH^- and H_2O, we also considered the effect of the basis sets on this molecular property,

TABLE 3: Parallel and Perpendicular Components of the OH^- Polarizability: Comparison with Other Values Available in the Literature; Values in au

year	basis[a]	SCF	MP2	MP4	CCSD(T)	MCPF	ref
				$\alpha_\parallel$			
1986	[7.5.3/5.3]	17.67					47
1988	[7.3.3/5.3]	17.7[b]	26.5	32.8			48
	[5.3.3/3.3]	18.3[b]	25.4	29.6			48
	EFV	18.6[b]	26.9	32.3			48
1988		18.95[c]					49
1990	[8.6.4.3/5.3.2](ANO)	18.61				26.82	50
1992	S=Pol1 [5.3.2/3.2]	16.96		27.88			51
2002	aug-cc-pVDZ	15.00	17.92	19.09	17.77		present work
	d-aug-cc-pVTZ	18.54	26.17	30.73	26.38		present work
	R-ANO [9.7.4.2/4.3.2]	18.40	25.17	28.45	24.85		present work
	S++f′2f,+d′2d	18.69	27.14	33.34	27.82		present work
				$\alpha_\perp$			
1986	[7.5.3/5.3]	20.81					47
1988	[7.3.3/5.3]	21.1[b]	40.4	53.5			48
	[5.3.3/3.3]	22.9[b]	40.0	49.8			48
	EFV	23.1[b]	42.0	54.3			48
1990	[8.6.4.3/5.3.2](ANO)	23.43				51.80	50
1992	S=Pol1 [5.3.2/3.2]	19.34		46.05			51
2002	aug-cc-pVDZ	15.43	23.09	25.88	23.53		present work
	d-aug-cc-pVTZ	23.09	40.49	50.42	42.72		present work
	R-ANO [9.7.4.2/4.3.2]	23.30	40.85	50.47	43.16		present work
	S++f′2f,+d′2d	23.22	42.73	56.70	46.67		present work

[a] The notation [*n*1.*n*2.../*m*1.*m*2...] refers to the contracted functions on oxygen (functions *n*) and hydrogen (functions *m*) atoms, respectively. [b] CHF calculations. [c] MCSCF calculations.

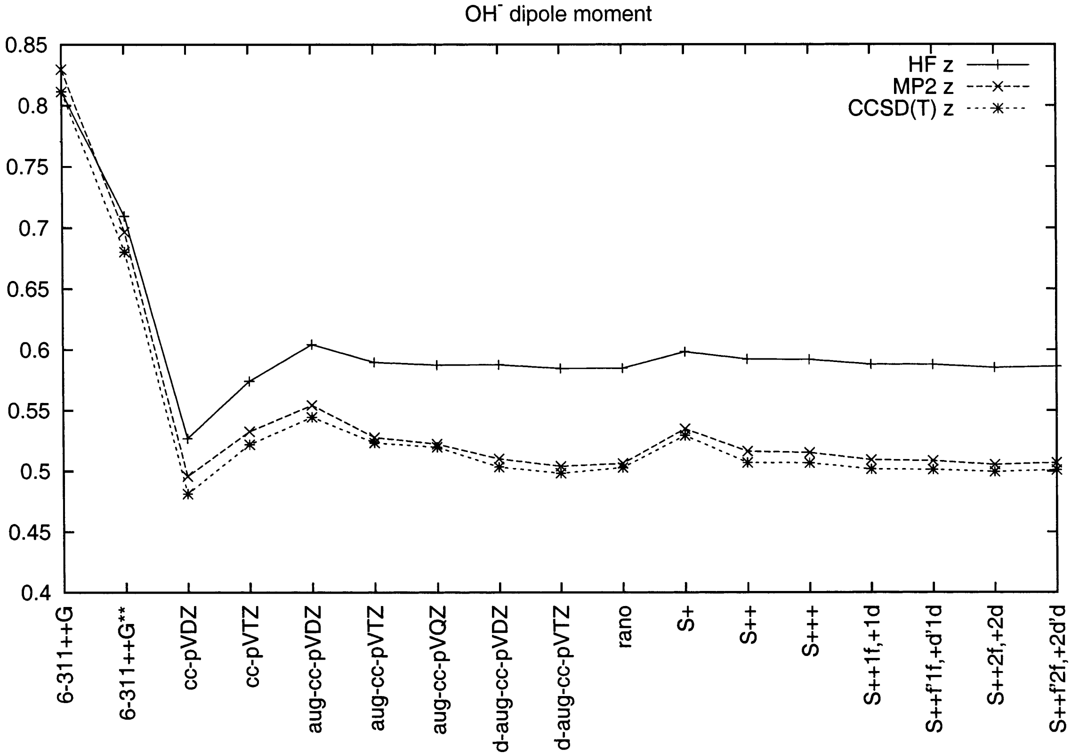

Figure 3. Dipole moment components of OH^- (in au, basis sets given in abscissa).

at various levels of the calculation. The results are gathered in Figures 3 and 4.

Most of the basis sets give the dipole moment of OH^- (Figure 3) within an accuracy of about 10%. Only the 6-311G series results are out of this range. The MP2 and CCSD(T) values are close. As previously noticed for the water polarizability, the aug-cc-pVDZ basis starts a plateau, a smooth transition being completed with the d-aug-cc-pVDZ basis. The S+ basis gives somewhat less better results than the other bases of this series. The agreement between the bases is generally quite good for the water molecule (Figure 4). The plateau now starts with the small cc-pVDZ basis and is completed with the aug-cc-pVDZ basis. Again, only the 6-311G series results are out of the plateau. The values obtained with basis S+ do not display a particular behavior; they are in complete agreement with the other values plotted in the plateau. Globally, the effect of the basis set on the dipole moments is similar to that described for the polarizability components, but the general agreement between the results given by all of the basis sets is considerably better.

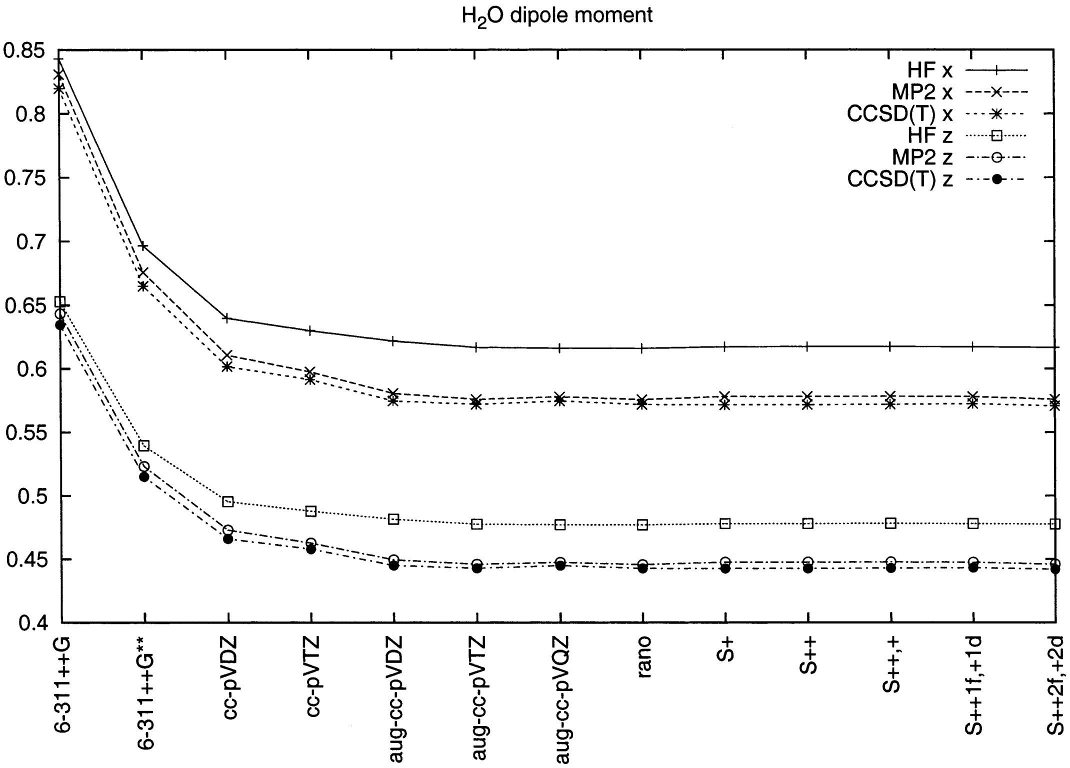

Figure 4. Dipole moment components of H_2O (in au, basis sets given in abscissa).

C. $OH^-(H_2O)$ System. For polar molecules, the dominant contributions to the intermolecular interactions are the electrostatic, induction, and dispersion terms. They are directly related to the dipole moments and polarizabilities of the subsystems. It is thus essential that these molecular properties are correctly described for both subsystems. However, other terms also contribute, especially the exchange ones, at any level of the perturbation expansion. Because some of these various contributions may have opposite signs, the final intermolecular energy is a subtle combination of several terms, such that compensation of errors may occur. Furthermore, as recalled in the Introduction, another important difficulty arises in the geometry optimization of intermolecular systems, due to the BSSE that leads to too attractive intermolecular energies associated with too short intermolecular distances. An obvious compensation of errors occurs if the polarizability of the subsystems is underestimated; the underestimated attractive induction and dispersion energies are counterbalanced by the attractive BSSE. Other cancellations of errors may also occur. For such reasons, it can happen that some basis sets, which do not give accurate polarizabilities, give nevertheless acceptable geometries of the $OH^-(H_2O)$ system.

Ab initio studies concerning the effect of the basis set on the binding of the $OH^-(H_2O)$ system appeared in the literature for years. The inclusion of diffuse functions and the correction of the BSSE were especially examined.[9,10,13−16,19,22−24,78,79] In most cases, several levels of calculation are available, the zero point energy (ZPE) correction is taken into account, and a value of ΔH is proposed. Globally, the binding energies obtained at the MP2 level vary from 26.8 to 28.6 kcal mol^{-1} without BSSE correction and from 23 to 26 kcal mol^{-1} when the counterpoise correction[52] is used. These results are obtained with Pople-type bases,[13,16,19,24,78] DZP bases,[14] or aug-cc-pVXZ bases.[15,14,24] Values issued from CCSD(T) and MP2 calculations are close.[24] MP4 calculations do not converge to CCSD(T) values.[24]

Our own purpose is somewhat different from these previous studies since our analysis of the $OH^-(H_2O)$ system bonding is closely related to that of the polarizability of the subsystems. Furthermore, we also examine the effect of the BSSE correction on the optimized geometry and not only on the energy. This point was never considered for this system. Several bases were thus selected, taking benefit of the analyses presented in Sections III.A,B. Two categories of bases were especially considered. Among those that do not properly describe the polarizability of OH^-, in particular the perpendicular component, we retained the aug-cc-pVDZ and aug-cc-pVTZ bases. Among the bases suitable for the polarizability, we retained the S series. This selection should be paradigmatic of the other bases.

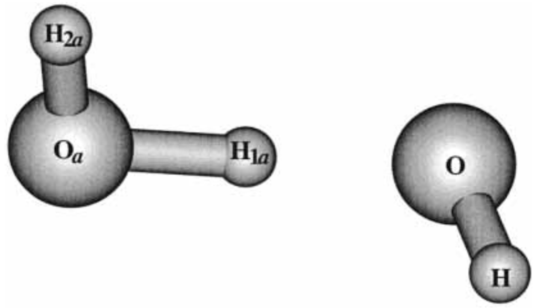

Figure 5. Most stable structure of the $OH^-(H_2O)$ system.[81]

A full optimization of the geometry was performed with the selected bases at the MP2 level. The most stable structure of $OH^-(H_2O)$ is shown in Figure 5. Bases S+, S++, and S++,+ give very close results for both the geometries and the energies. On the other hand, bases S++1f,+1d, S++f′2f,+2d, and S++2f,+2d also lead to very similar values. For this reason, only the calculations using bases S+ and S++2f,+2d are reported in Table 4 for the S series. In each case, two geometry optimizations were performed, considering either the uncorrected or the BSSE-corrected potential surface. Both the geometric parameters and the corresponding energetic results are gathered in Table 4.

TABLE 4: Internal Coordinates of $OH^{-}H_2O$ Fully Optimized at the MP2 Level, Best Estimates for the Binding Energy (D_e), Dissociation Energy (D_0), and Enthalpy of Formation (ΔH (298 K)), Calculated with Different Basis Sets; Distances in Ångstroms, Angles in Degrees, and Energies in kcal mol^{-1}

	S+		S++2f,+2d		aug-cc-pVDZ		aug-cc-pVTZ	
r(O−H)	0.972[a]	0.972[b]	0.970	0.970	0.969	0.970	0.963	0.964
r(O−H_{1a})	1.391	1.447	1.368	1.429	1.424	1.473	1.363	1.433
r(O_a−O)	2.495	2.533	2.480	2.519	2.513	2.548	2.476	2.514
r(O_a−H_{1a})	1.104	1.086	1.112	1.091	1.090	1.076	1.113	1.082
r(O_a−H_{2a})	0.968	0.969	0.968	0.967	0.966	0.965	0.961	0.961
α(O−H_{1a}−O_a)	178.53	177.24	177.42	177.19	177.10	176.70	177.92	176.54
α(H_{1a}−O_a−H_{2a})	101.54	101.28	101.11	101.31	101.42	101.44	101.88	101.82
α(H_{1a}−O−H)	104.94	105.16	104.12	105.17	106.14	106.59	104.95	106.20
δ(H−O−O_a−H_{2a})	102.20	102.41	98.51	102.13	101.04	102.02	101.47	101.70
$E_{\text{int}}^{\text{MP2}}$	−33.009	−31.288	−35.181	−32.717	−31.713	−30.381	−35.146	−32.635
$E_{\text{int}}^{\text{CCSD(T)}}$	−32.541	−30.938	−34.998	−32.661	−31.496	−30.247	−35.899	−32.801
BSSE(MP2)	3.834	3.689	4.713	4.507	2.053	1.931	1.326	1.202
BSSE(CCSD(T))	3.977	3.827	4.648	4.449	2.251	2.123	1.292	1.778
$E_{\text{relax}}^{\text{CCSD(T)}}$	7.939	6.183	9.286	6.776	6.867	5.496	9.835	6.627
D_e	−24.601	−24.755	−25.712	−25.885	−24.629	−24.747	−26.064	−26.171
$\Delta E_{\text{ZPE}}^{\text{MP2}}$	1.000		0.805		1.062		0.710	
D_0	−23.601	(−23.755)[c]	−24.907	(−25.080)	−23.567	(−23.685)	−25.354	(−25.461)
T effect	1.222		1.265		1.203		1.212	
ΔH (298 K)	−24.823	(−24.977)[d]	−26.171	(−26.345)	−24.770	(−24.888)	−26.566	(−26.673)

[a] Uncorrected geometry. [b] BSSE-corrected geometry. [c] Using the values of $\Delta E_{\text{ZPE}}^{\text{MP2}}$ computed for the BSSE-uncorrected geometries. [d] Using the values of the temperature effect computed for the BSSE-uncorrected geometries.

For a given basis set, the MP2 and CCSD(T) values of the BSSE are close. They are similar for the uncorrected or BSSE-corrected geometries. It is not surprising that they are much larger with the S bases than with the aug-cc-pVXZ series, due to more diffuse functions included in the former. Unexpectedly, the changes induced in the geometry by the BSSE correction are rather similar for all bases. The main changes occur in the geometric parameters involving the H bond. The BSSE correction lengthens the intermolecular O−O distance by about 0.04 au. Indeed, the much larger lengthening of the distance r(O−H_{1a}) between the oxygen atom of OH^- and the H atom of the water molecule (which can reach 0.07 au) is counterbalanced by the shortening (up to 0.03 au) of the OH bond length of the water molecule, r(O_a−H_{1a}). Clearly, the OH bond of the water molecule is overlengthened when the BSSE is not corrected in the geometry optimization process. We can remark that the uncorrected geometry obtained with the aug-cc-pVDZ basis is very close to the BSSE-corrected geometry given by the S++2f,+2d basis. Because the aug-cc-pVDZ basis underestimates the dispersion energy (Figure 2), this good agreement is due to cancellation of errors.

The BSSE-corrected CCSD(T) and MP2 intermolecular energies, $E_{\text{int}}^{\text{CCSD(T)}}$ and $E_{\text{int}}^{\text{MP2}}$, are generally close, as previously noted in the literature.[24] In the worst case (Basis aug-cc-pVTZ, uncorrected geometry), the difference is about 0.7 kcal mol^{-1}. This difference is much smaller for the BSSE-corrected geometries than for the uncorrected ones. The relaxation energy, $E_{\text{relax}}^{\text{CCSD(T)}}$, due to the change of the geometry of the subsystems in the total system with respect to that of the isolated molecules, may be large: up to 9.8 kcal mol^{-1} for uncorrected geometries. As expected from our analysis of the BSSE effect on the optimized geometries, the relaxation energy is smaller for the BSSE-corrected geometries. We may note that the relaxation energy obtained with basis S++2f,+2d and the BSSE-corrected geometry is quite close to that obtained with basis aug-cc-pVDZ and the uncorrected geometry. This confirms the hypothesis of cancellation of errors mentioned above.

The intermolecular energies $E_{\text{int}}^{\text{CCSD(T)}}$ and $E_{\text{int}}^{\text{MP2}}$ significantly depend on both the basis set and the geometry optimization. The CCSD(T) values vary from 30.247 to 35.899 kcal mol^{-1}. The difference (5.65 kcal mol^{-1}) represents about 16% of the best value. The effect due to the optimization of the geometry may reach 3 kcal mol^{-1} (aug-cc-pVTZ basis). However, when the relaxation energy is taken into account, the largest error on the values of D_e (1.58 kcal mol^{-1}, from 24.60 to 26.17 kcal mol^{-1}) represents only 6% of the best value. In fact, D_e is hardly sensitive to the BSSE correction of the geometry, and the difference is due to the basis set. These values have been corrected for the ZPE, ΔE_{ZPE}, and the temperature effect (denoted by "*T* effect" in Table 4) to obtain D_0 and ΔH (298 K). Because of the close general agreement between the CCSD(T) and the MP2 calculations, we used the MP2 values of these correction terms. The values of $\Delta E_{\text{ZPE}}^{\text{MP2}}$ are about 1 kcal mol^{-1} with bases S+ and aug-cc-pVDZ, hardly smaller with the larger bases. They are in agreement with those reported in the literature.[14,15,19] The temperature effect is about 1.2 kcal mol^{-1} with any basis, again in agreement with the value proposed in ref 15. For these reasons, D_0 and ΔH (298 K) follow the same pattern as D_e. Furthermore, because $\Delta E_{\text{ZPE}}^{\text{MP2}}$ and the temperature effect nearly quench each other, as also found in the literature,[15,16,23] the values of D_e and ΔH (298 K) are very close. Given the stability of the corrections due to $\Delta E_{\text{ZPE}}^{\text{MP2}}$ and to the temperature effect, we did not recompute these terms for the BSSE-corrected geometry; the values of D_0 and ΔH (298 K) are thus given in parentheses for such geometries. From this analysis, it seems reasonable to assume that the value of ΔH at 298 K lies around 26.4−26.7 kcal mol^{-1}, in agreement with the most recent measurements (26.5 ± 1.0 kcal mol^{-1}) of Meot-Ner and Speller.[80] Our theoretical value is also very close with the CBS limit of 26.6 kcal mol^{-1} proposed in ref 24. It is worth noting that cancellations of errors may artificially lead to good results; the neglect of the BSSE in both the energy and the geometry optimization, counterbalanced by an underestimated dispersion energy, gives 27 kcal mol^{-1} with the aug-cc-pVDZ basis.[15]

IV. Conclusions

Strictly, a good description of the full system requires the molecular properties of the subsystems that play a role in the intermolecular interaction to be correctly described. Considering both the subsystems and the full system, we examined, as a joint study, the accuracy reachable on the molecular properties and the consequence on the description of the full system. This lead us to focus the attention on the role of some cancellation of errors in ab initio calculations. Following this approach of the problem, the choice of the basis set, of particular importance, was discussed in detail. The basis set effect occurs in the description of the molecular properties and, consequently, on the energetic contributions to the stabilization of the full system. However, it also occurs in the geometry optimization. We recall the main features of this study.

Molecular Properties. The dipole moment and static dipole polarizability of the subsystems were considered. We examined the effect of three different factors on the accuracy of these molecular properties: the level of the electron correlation calculations, the method used to compute the molecular polarizability components, and the basis set. Calculations were performed at the HF, MP*n*, and CCSD(T) levels. The polarizability components were computed either from the analytical formulas or from the finite field method. In this last case, parabolic and quartic polynomials fits were compared. Four series of basis sets, built from four initial sets extended with polarization and diffuse functions, lead to 15 or so bases. The most delicate treatment occurs with the polarizability of the hydroxide anion. The main conclusions concerning the study of the molecular properties are the following:

(i) Whatever the basis set, the MP*n* series exhibits an oscillatory pattern and its convergence is dubious. The MP4 results do not converge to the CCSD(T) values.

(ii) For both subsystems, the MP2 and CCSD(T) values of the dipole moments are close. The MP2 and CCSD(T) values are also close for the water polarizability components and for the parallel polarizability component of OH^-. However, the MP2 perpendicular polarizability components of OH^- are significantly smaller than the CCSD(T) ones.

(iii) The description of the polarizability requires diffuse polarization functions. The Pople-type and the cc-pVXZ series are not suitable for any of the subsystems.

(iv) A correct description of the polarizability of OH^- requires more diffuse polarization functions than that of water. For instance, the aug-cc-pVXZ series gives acceptable values of the water polarizability (although significantly underestimated in the case of the aug-cc-pVDZ basis) but fails for OH^-. In the S series, the S+ basis results are correct for the water polarizability components but too small for the hydroxide ion. The other bases of the S series give hydroxide ion polarizability components in the same range but somewhat larger than those obtained with the d-aug-cc-pVXZ (X = D, T). It looks probable that a d-aug-cc-pVQZ basis would improve the agreement, but its cost would be much higher than that of the S++ type bases.

(v) The calculations published in previous papers on the OH^- polarizability were obtained, in the best case, at the MP4 level. Given our discussion on the convergence of this series, we expect our present results, based on the CCSD(T) method and using the finite field approach with a quartic polynomials fit, to be more accurate. Our recommended values, 27.8 au for the parallel and 46.7 au for the perpendicular polarizability components, look reasonable.

Geometry and Energetics of the $OH^-(H_2O)$ System, the Role of Cancellation of Errors. Concerning the $OH^-(H_2O)$ system, geometry optimizations were performed, corrected or not for the BSSE. The corresponding energetic data are discussed. In the second part of the work, the role of cancellation of errors is underlined. The main conclusions are the following:

(i) The BSSE is large with the diffuse basis sets needed for accurate polarizability; consequently the uncorrected geometry obtained with such bases underestimates the intermolecular distance and overestimates the length of the water OH bond involved in the H-bond.

(ii) The geometric relaxation energy of the subsystems when they form the total system may be quite large (up to 9.8 kcal mol^{-1}). It depends on the basis set and is smaller when the geometry is BSSE-corrected.

(iii) When the relaxation energy is taken into account, D_e is quite similar for the uncorrected and BSSE-corrected geometries. This also holds for D_0 and ΔH (298 K). Furthermore the discrepancies due to the basis sets are smoothed. The value of ΔH at 298 K lies around 26.4−26.7 kcal mol^{-1}, in excellent agreement with the most recent experimental results (26.5 ± 1.0 kcal mol^{-1} [80]).

(iv) Because of artificial cancellation of errors, the uncorrected geometry given by the aug-cc-pVDZ basis is quite close to the BSSE-corrected geometry obtained with our best basis: at the minimum, the overestimation of the attractive energy due to the BSSE artificially compensates the underestimation of the dispersion energy arising from the aug-cc-pVDZ polarizability. As a consequence, the BSSE-uncorrected geometry and BSSE-uncorrected intermolecular energy are fortuitously in the range of the best BSSE-corrected ones.

(v) Given the nature of artificial cancellation of errors, it is delicate to a priori guess if a basis, which does not correctly describe the polarizability components, nevertheless gives acceptable geometries and energetics of the full system by neglecting the BSSE corrections. Only the comparison with accurate results can answer this question.

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