

Ab initio studies of the structures and energies of the $\text{H}^-(\text{H}_2\text{O})$ and $\text{H}^-(\text{H}_2\text{O})_2$ complexes

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Accurate calculations for the $\text{H}^-(\text{H}_2\text{O})$ complex with extended basis sets are reported at the restricted Hartree-Fock (RHF) through the fourth-order Møller-Plesset (MP) perturbation levels of theory. In the equilibrium geometry of the $\text{H}^-(\text{H}_2\text{O})$ complex the H^- anion is found to lie almost along one of the H-O bond directions. The H-H⁻ distance proved to be very sensitive to electron correlation effects: it is 1.8 and 1.4 Å at the RHF and MP2 levels, respectively. The interaction energy between H^- and H_2O at the MP4 level including counterpoise corrections for basis set superposition error, depending upon the basis set used, is found to range from 16.2 to 16.9 kcal/mol, and the electron correlation is responsible for one-third of this value. The enthalpy of formation of $\text{H}^-(\text{H}_2\text{O})$ is estimated to be from -15.2 to -16.0 kcal/mol compared with the experimental value of -17.3 ± 1.2 kcal/mol. The vibrational frequencies of $\text{H}^-(\text{H}_2\text{O})$ are also reported. The $\text{H}^-(\text{H}_2\text{O})_2$ complex is also studied by using a polarized double zeta basis set. The geometry of the $\text{H}^-(\text{H}_2\text{O})_2$ complex is partly optimized at the MP2 level and the energetic effects of the addition of the second water to $\text{H}^-(\text{H}_2\text{O})$ are analyzed.

I. INTRODUCTION

Recent investigations by Nibbering and co-workers¹ as well as Paulson and Henschman² provided, by means of mass-spectroscopy, convincing evidence that H_3O^- is a relatively long-lived species. In addition, Paulson and Henschman estimated the binding energy of the H_3O^- complex to be 17.3 ± 1.2 kcal/mol with respect to dissociation to $\text{H}^- + \text{H}_2\text{O}$ and 6.9 ± 1.2 kcal/mol with respect to dissociation to $\text{OH}^- + \text{H}_2$. There is also evidence (Ambruster *et al.*³) that larger clusters also exist; in particular, $\text{H}^-(\text{H}_2\text{O})_5$ and $\text{H}^-(\text{H}_2\text{O})_{11}$ have been observed.

From our perspective, the importance of H_3O^- is twofold. First, it serves as a model for negative ion-water complexes. Second, it may be viewed as an intermediate in the reaction



which was the first example reported of a negative ion-molecule reaction.⁴ Therefore, by studying H_3O^- we may understand better some elements of the proton-transfer process.

Despite the clear importance of H_3O^- , very few theoretical investigations on H_3O^- can be found in the literature. The earliest studies (Kari and Csizmadia⁵ and Glidwell⁶ predicted that H_3O^- should be unstable with respect to $\text{H}^- + \text{H}_2\text{O}$. Recently, Squires⁷ reported SCF calculations with full geometry optimization (4-31 + G basis) plus electron correlation corrections at the second-order Møller-Plesset (MP2) level. He found a binding energy in $\text{H}^-(\text{H}_2\text{O})$ of 15.6 kcal/mol [hereafter the symbol $\text{H}^-(\text{H}_2\text{O})$ will denote the $\text{H}^- \cdots \text{H}_2\text{O}$ form of H_3O^- and

$\text{OH}^-(\text{H}_2)$ will denote the $\text{OH}^- \cdots \text{H}_2$ form of H_3O^-]. Moreover, he noticed only small changes in the binding energy when he allowed for correlation effects. His optimized r_{HH} distance at the SCF level was 1.79 Å (cf. Fig. 1, bent configuration) and r_{OH} was 0.98 Å.

A more extensive treatment of H_3O^- has been published by Cremer and Kraka.⁸ The optimization of geometry was carried out at both the SCF level (6-31G* basis) and MP2 level (6-31 + + G** basis) and yielded $r_{\text{HH}} = 1.508$ and 1.479 Å, respectively. Note that their r_{HH} differs substantially from Squire's SCF result. Cremer and Kraka report a binding energy of 26 kcal/mol (in the abstract) but from their absolute energies (see Table II in Ref. 8) one obtains 29.9 kcal/mol in the SCF/6-31G*/SCF6-31G* calculations and 18.7 kcal/mol in the MP2/6-31 + + G**/MP2/6-31 + + G** calculations (there exists then some confusion in our minds about what they actually are reporting). The correlation contributions to both the binding energy and geometry are, hence, not small. The energetics of the dissociation into $\text{OH}^- + \text{H}_2$ was also studied by Cremer and Kraka; they estimated $\text{OH}^- + \text{H}_2$ to be 4.8* kcal/mol less stable than $\text{H}^- + \text{H}_2\text{O}$ and the $\text{OH}^-(\text{H}_2)$ complex to be bound by 4.8 kcal/mol relative to $\text{OH}^- + \text{H}_2$.

Both Squires and Cremer and Kraka focused on qualitative aspects of the existence and dissociation of H_3O^- . Standard Pople and co-workers basis sets⁹ were used, as a result of which, their absolute energies were not highly accurate. Moreover, there are some aspects of the results of their calculations which are intriguing and demand further investigation. The first is that the r_{HH} distance is probably very sensitive to the basis set and to the correlation method used. Potential surfaces of anion-water complexes are known to require good accuracy to achieve reliable description. The

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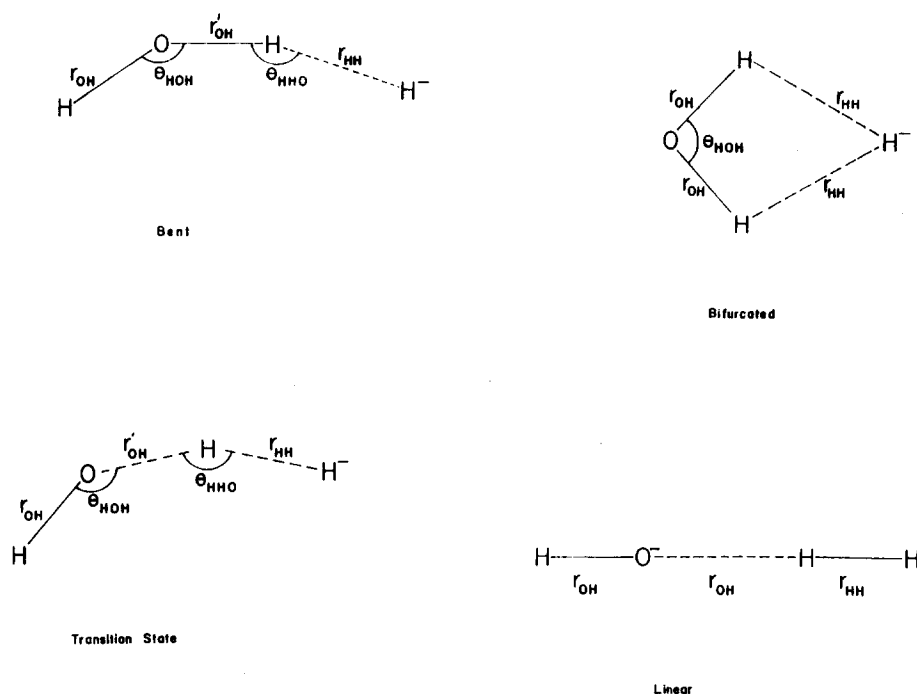


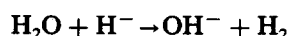
FIG. 1. Configurations of the H_3O^- complex considered in this work.

second is that the correlation energy appears to be quite important in determining the binding energy reported in the results of Ref. 8. If so, more attention should be paid to the selection of both the correlation method and to the choice of basis sets. Therefore, to provide more *qualitative* results for H_3O^- and to understand better the nature of negative ion-water complex, it is important to carry out calculations with extended basis sets and to include correlation beyond the MP2 level. Accounting for basis set superposition error (BSSE) is also very important because the H^- ion, due to its diffuse charge cloud, has been shown to be very BSSE-prone even in the SCF-level calculations.¹⁰ Consequently, the use of basis sets without diffuse functions (e.g., the 6-31G* basis used in the SCF calculations of Cremer and Kraka) is expected to lead to huge BSSE (in fact, we found that BSSE amounts to ~ 20 kcal/mol for the SCF/6-31G* results). Moreover, the elimination of BSSE at the correlated level is much more difficult^{11,12} than at the SCF level.

In this paper, accurate calculations for the $\text{H}^-(\text{H}_2\text{O})$ and $\text{H}^-(\text{H}_2\text{O})_2$ complexes, with extended basis sets at the fourth-order Møller-Plesset (MP4)¹³ level are reported. The GAUSSIAN 82 code^{14,15} on the San Diego CRAY X-MP was used for all of the calculations reported here. In Sec. II the details used in our evaluation of interaction energies by means of the supermolecular MP4 approach are outlined. Particular attention is paid to the application of the Boys and Bernardi counter-poise (CP)¹⁶ method for treating BSSE in the case when the monomer geometries become distorted in the complex. This problem of geometry relaxation is important for fairly strong interaction complexes, $\text{H}^-(\text{H}_2\text{O})$ being a representative example.

In Sec. III the calculations for $\text{H}^-(\text{H}_2\text{O})$ are described and discussed. When choosing basis sets (Sec. III A) particular attention was paid to ensuring proper description of the H_2O properties as well as of the diffuse electron charge at the H^- ion. The geometry of $\text{H}^-(\text{H}_2\text{O})$ was fully optimized at

the SCF and MP2 levels (Sec. III B). A significant shortening of the $\text{H}\cdots\text{H}^-$ distance (by 0.4 \AA) was found after allowing for electron correlation at the MP2 level. The equilibrium geometry optimized at the MP2 level did not change significantly at the MP4 level nor was it much affected by the BSSE. The electron correlation contribution to the interaction energy was also found to be important [approximately one-third of the total interaction energy at the equilibrium distance (Sec. III C)]. Harmonic frequencies of $\text{H}^-(\text{H}_2\text{O})$ were computed and compared with those for isolated H_2O . In Sec. III D, ΔH_f^{298} for the formation of $\text{H}^-(\text{H}_2\text{O})$ was evaluated and found to be close to the experimental value. The energetics of the proton transfer reaction



was analyzed. The transition state connecting $\text{H}^-(\text{H}_2\text{O})$ and $\text{OH}^-(\text{H}_2)$ as well as the energies of the $\text{OH}^-(\text{H}_2)$ complex and the $\text{OH}^- + \text{H}_2$ products were also computed.

In Sec. IV the results for $\text{H}^-(\text{H}_2\text{O})_2$ are presented. They include the results of geometry optimization and the analysis of individual contribution to the interaction energy (one-, two-, and three-body). The energies for loss of the first water molecule was found to be slightly smaller (by 0.5 kcal/mol) than for the loss of the second one.

II. INTERACTION ENERGY DECOMPOSITION METHOD

Calculations of intermolecular interactions by means of MPPT offer several advantages in comparison with other methods. As shown by Dierksen *et al.* on the difficult Be_2 system,¹⁷ a complete fourth-order MPPT calculation may recover a sufficient portion of the pertinent electron correlation effects, leading at the same time to size-consistent results. Very high-order and highly accurate calculations of Handy *et al.*¹⁸ confirmed that, unless bond breaking or curve crossings occur, the MPPT series is well convergent and then quite reliable. Furthermore, many valuable qualitative

and even quantitative results may be already obtained at lower than the fourth-order level using standard basis sets. As shown by Kestner *et al.*¹⁹ and Szczesniak and Scheiner,²⁰ if the BSSE is corrected for, the MP2 and MP3 levels can successfully be applied to study hydrogen bonded systems. It should be emphasized here that because of the relatively simple expressions, in particular for $E^{(2)}$ and $E^{(3)}$,¹³ the computer codes can be easily vectorized to yield high performance on supercomputers and applied even for such large systems as the nitromethane dimer.²¹ It is also important to note that the second- and third-order corrections to the interaction energy may be asymptotically related to physically meaningful contributions to the interaction energy derived from the classic Rayleigh-Schrodinger (RS) perturbation theory of intermolecular forces.²²

The method used in the calculations presented in this paper is the complete fourth-order MPPT,¹³ implemented in the GAUSSIAN 82 code.^{14,15} All contributions to the total energy through fourth-order in the electron correlation perturbation [i.e., those due to single (*S*), double (*D*), triple (*T*) and quadruple (*Q*) substitutions in the reference HF determinant] are included.

A. The interaction energy decomposition

The interaction energy arising among *N* species, *A*, *B*,... and *Z*, at the *i*th order and through the *i*th order of MPPT is defined as follows

$$\Delta E_{AB...Z}^{(i)} = E_{AB...Z;G_{AB...Z}}^{(i)} - \sum_{X=A,B,...,Z} E_{X;G_X}^{(i)}, \quad (1a)$$

$$\Delta E_{AB...Z}(i) = \sum_{k=0}^i \Delta E_{AB...Z}^{(k)}, \quad (1b)$$

respectively. Here, $E_{AB...Z;G_{AB...Z}}^{(i)}$ and $E_{X;G_X}^{(i)}$ denote the energies of complex *AB...Z* and its component *X*, respectively. Since the geometries of the subspecies may relax (distort) in the complex, the subscripts $G_{AB...Z}$ and G_X denote the relaxed and isolated-species geometries, respectively. Note, that the SCF interaction energy is the sum of the zeroth- and first-order MPPT energy differences

$$\Delta E_{AB...Z}^{\text{SCF}} = \Delta E_{AB...Z}^{(0)} + \Delta E_{AB...Z}^{(1)} = \Delta E_{AB...Z}(1). \quad (2)$$

It is convenient to write the total energy of the complex *AB...Z* in the form of a many-body expansion²³

$$E_{AB...Z;G_{AB...Z}}^{(i)} = \sum_X E_{X;G_X}^{(i)} + \sum_X \tilde{\Delta E}_X^{(i)} + \sum_{X>Y} \tilde{\Delta E}_{XY}^{(i)} + \sum_{X>Y>W} \tilde{\Delta E}_{XYW}^{(i)} + \cdots \tilde{\Delta E}_{AB...Z}^{(i)},$$

where

$$X, Y, W = A, B, \dots, Z. \quad (3)$$

The terms in Eq. (3) have clear physical interpretation. The one-body term $\tilde{\Delta E}_X^{(i)}$ includes the effect of the relaxation of *X*'s geometry in the complex. It is defined as

$$\tilde{\Delta E}_X^{(i)} = E_{X;G_{AB...Z}}^{(i)} - E_{X;G_X}^{(i)}, \quad (4)$$

where $E_{X;G_{AB...Z}}^{(i)}$ denotes $E_X^{(i)}$ evaluated at the geometry which *X* assumes within complex *AB...Z*.

The two-body term $\tilde{\Delta E}_{CD}^{(i)}$ represents the pair-wise in-

teraction between two monomers *C* and *D* in their relaxed geometries and in the configuration that they assume within complex *AB...Z*:

$$\tilde{\Delta E}_{CD}^{(i)} = E_{CD;G_{AB...Z}}^{(i)} - \sum_{X=C,D} E_{X;G_{AB...Z}}^{(i)}. \quad (5)$$

Higher many-body terms are defined recursively; for example,

$$\tilde{\Delta E}_{CDF}^{(i)} = E_{CDF;G_{AB...Z}}^{(i)} - \sum_{X=C,D,F} E_{X;G_{AB...Z}}^{(i)} - \sum_{X>Y} \tilde{\Delta E}_{XY}^{(i)}. \quad (6)$$

$\tilde{\Delta E}_{CDF}^{(i)}$ is a three-body contribution arising between relaxed-geometry monomers arranged in the same configuration as they have in the complex. Besides the physical interpretation, the partitioning of Eq. (3) has a practical advantage. The absolute energies of the many-body subsystems which are subtracted in Eqs. (5) and (6) are orders of magnitude larger than the interaction energies. Since the BSSE must be taken care of in all finite basis calculations, it is quite convenient (see later) to subtract the energies which are obtained at the same geometries.

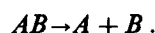
The total interaction energy in a two-body system *AB* may therefore be defined as

$$\Delta E_{AB}^{(i)} = \tilde{\Delta E}_A^{(i)} + \tilde{\Delta E}_B^{(i)} + \tilde{\Delta E}_{AB}^{(i)}. \quad (7)$$

Likewise for the three-body system *ABC*,

$$\Delta E_{ABC}^{(i)} = \tilde{\Delta E}_A^{(i)} + \tilde{\Delta E}_B^{(i)} + \tilde{\Delta E}_C^{(i)} + \tilde{\Delta E}_{AB}^{(i)} + \tilde{\Delta E}_{BC}^{(i)} + \tilde{\Delta E}_{AC}^{(i)} + \tilde{\Delta E}_{ABC}^{(i)}. \quad (8)$$

Besides the interaction energies given in Eqs. (7) and (8), it is often interesting to compare the energies for sequential loss of various fragments:



For the dissociation of a three-body system *ABC* we have

$$\Delta E_{ABC \rightarrow AB}^{(i)} = \tilde{\Delta E}_{AC}^{(i)} + \tilde{\Delta E}_{BC}^{(i)} + \tilde{\Delta E}_{ABC}^{(i)} + \tilde{\Delta E}_C^{(i)} + DE_{AB}^{(i)}, \quad (9)$$

where $DE_{AB}^{(i)}$ denotes the energy change due to the relaxation of the geometry of subunit *AB* caused by the removal of *C*:

$$DE_{AB}^{(i)} = E_{AB;G_{ABC}}^{(i)} - E_{AB;G_{AB}}^{(i)}. \quad (10)$$

Likewise for *AB* → *A* + *B*,

$$\Delta E_{AB \rightarrow B}^{(i)} = \tilde{\Delta E}_{AB}^{(i)} + \tilde{\Delta E}_A^{(i)} + \tilde{\Delta E}_B^{(i)} - DE_{AB}^{(i)}. \quad (11)$$

B. Basis set superposition error decomposition

As has been mentioned above, when the energies of super-molecule *AB...Z* and its components are calculated with finite basis sets the use of Eqs. (5) and (6) involves BSSE. To evaluate the two-, three-, and many-body interaction energy terms, a generalization of the Boys and Bernardi CP method¹⁶ may be straightforwardly used. Within this CP method all of the energies in Eqs. (5) and (6) have to be

computed with the basis set of the *whole complex* ($\chi_A \cup \chi_B \cup \dots \cup \chi_Z$, where χ_C denotes the basis of C), see also Bulski.²⁴ This approach ensures a basis-set-consistent calculation of all the terms entering Eqs. (5) and (6) [although it does not remove the basis set extension (BSE) effect on the interaction energy^{25,12}]. As to the one-body term ($\tilde{\Delta}E_X$), it may be evaluated separately with the basis set of X only, since this does not lead to any basis set inconsistency in the subtraction in Eq. (4) (cf. also van Lenthe *et al.*²⁶ and Ref. 27). The BSSE's for the monomer, dimer, etc., energies are defined as follows:

$$\delta_X^{(i)} = E_X^{(i)}(\chi_A \cup \chi_B \cup \dots \cup \chi_Z) - E_X^{(i)}(\chi_X), \quad (12)$$

$$\delta_{XY}^{(i)} = E_{XY}^{(i)}(\chi_A \cup \chi_B \cup \dots \cup \chi_Z) - E_{XY}^{(i)}(\chi_X \cup \chi_Y), \quad (13)$$

etc. Later in the text we will also use the symbol δ without the specification of X in which case it represents the total effect

$$\delta^{(i)} = \sum_{X=A,B,\dots,Z} \delta_X^{(i)}. \quad (14)$$

It should be stressed that correcting only for $\delta_X^{(i)}$ and assuming $\delta_{XY}^{(i)}$, $\delta_{XYZ}^{(i)}$, etc. negligible has not generally proven to yield reliable estimation of BSSE (Wilson *et al.*²⁸).

As to whether one should use a "full" or a "virtuals-only" CP correction, a number of both theoretical and numerical arguments have been recently presented in favor of the full approach.^{12,25} First, an argument commonly raised against the full CP correction, that the monomers in the dimer cannot access the occupied orbitals of the partner because of the Pauli Exclusion Principle, was shown to be misinterpreted, cf. Gutowski *et al.*²⁵ Second, for the model He_2 system, if a systematic sequence of basis sets was used, the full CP-corrected results were shown to converge smoothly to the exact results, both at the SCF²⁵ and correlated levels.¹² In contrast to the full CP method, the virtuals-only modifi-

cation revealed an irregular behavior and occasionally yielded nonsensical results. Better performance of the full correction was also demonstrated for the water dimer.²⁰

III. $\text{H}^-(\text{H}_2\text{O})$

A. Basis sets

Detailed descriptions of the basis sets used in this work are given in Table I. The basis set for oxygen was taken from Dacre.²⁹ It is essentially the basis of Clementi and Popkie,³⁰ except that its p orbitals are less contracted, and additional diffuse orbitals have been included to improve the computed dipole moment and the polarizability of the water molecule. Since the basis set for H should be flexible enough to describe both the H atom in H_2O and the H^- ion, the basis of Dacre was not used. Instead, two other sets were investigated, giving rise to the two bases for water which we label bases A and B . The A set includes the H atom basis $[7s2p/4s2p]$ of Diercksen and Sadlej^{31,32} determined in their studies of electric properties of H_2 and first row hydrides (cf. the references in Ref. 32). It contains diffuse s functions. Set B includes the H atom basis of Lie and Clementi (s set)³³ augmented with one diffuse s and four polarization p functions optimized by Adams³⁴ to reproduce the correlation energies of H_2 and of H^- (see Ref. 35 on H_3^- for details). Finally, basis set A^* was created by adding to basis A the following polarization functions: $f(0.18)$ at the O atom (from Ref. 36) and $d(0.075)$ at the H atom (from Ref. 32).

Bases A , A^* , and B were too large to be used in our $\text{H}^-(\text{H}_2\text{O})_2$ calculations. For $\text{H}^-(\text{H}_2\text{O})_2$, the C basis was used; it is of polarized double-zeta quality and was used by Szczesniak and Scheiner²⁰ for the water dimer (basis D_3 of Ref. 20). It was augmented with one diffuse s orbital with exponent 0.03 at H^- (as suggested by Clark *et al.*³⁷).

TABLE I. Description of basis sets for O and H. Energies in Hartrees, exponents in a_0^{-2} .

Label	Description of the basis	Method	Monomer energies	
			H_2O^a	H^-
A	O: $[12s8p2d/5s8p2d]$ basis from Table III in Ref. 29	SCF	-76.056 662	-0.487 517
		MP2	-76.282 172	-0.512 189
	H: $[7s2p/4s2p]$ basis from Table I in Ref. 32	MP4	-76.295 218	-0.522 297
A^*	O: the same as in basis A plus $1f(0.18)$	SCF	-76.056 839	-0.487 517
		MP2	-76.284 063	-0.512 721
	H: the same as in basis A plus $1d(0.075)$	MP4	-76.297 303	-0.522 677
B	O: the same as in basis A	SCF	-76.059 574	-0.487 787
	H: $[10s4p/6s4p]$ basis from Table I in Ref. 35	MP2	-76.289 159	-0.514 361
		MP4	-76.302 159	-0.524 655
C	O: $[11s7p2d/4s3p2d]^b$	SCF	-76.051 138	-0.483 814
	H: $[6s1p/2s1p]^b$	MP2	-76.263 096	-0.506 973
	H^- : as for H plus $s(0.03)^c$	MP4	-76.275 732	-0.517 060

^a The water geometry was: $r_{\text{OH}} = 0.964 \text{ \AA}$, $\theta_{\text{HOH}} = 105.5^\circ$. The correlated energies refer to the frozen core approximation.

^b Basis used by Szczesniak and Scheiner, basis D_3 in Ref. 20.

^c Suggested by Clark *et al.* (Ref. 37).

B. Optimization of geometry

Optimization of the geometry of the clusters was carried out with the *A* basis at SCF and MP2 levels by means of gradient and second derivative methods³⁸ implemented in the GAUSSIAN 82^{14,15} codes. The *A* basis was chosen because optimization of geometry with basis *B* would have been much more time consuming and the *B* basis was introduced at the later stages of this work. The optimized geometries are given in Table II. In agreement with Cremer and Kraka,⁸ our optimal geometry is "bent" (i.e., it has an OHH^- angle not equal to 180°). It is worthwhile to note here that, from considerations of electrostatic interactions only, the "bifurcated" geometry (with the H^- situated equidistant between the two H atoms of H_2O) should be the most favorable. In fact, we and Cremer and Kraka⁸ both find a local minimum for the latter configuration lying only 3 kcal/mol higher than the bent minimum. Since our bent (global) minimum is about 17 kcal/mol below the energy of $\text{H}_2\text{O} + \text{H}^-$, the potential energy surface is fairly flat by conventional chemical bond strength standards which is somewhat typical of anion-water complexes.

In addition to the above observations concerning the stable geometry of $\text{H}^- (\text{H}_2\text{O})$, we found the following results from analyzing our computational data:

(A) The interaction between H^- and H_2O deforms the water molecule; the HOH angle closes by a few degrees, the OH bond directed to H^- elongates slightly (by 0.073 Å at the MP2 level) and the other OH bond shortens slightly (by 0.002 Å). This deformation brings about a nonnegligible contribution to the interaction energy amounting to some 3 kcal/mol (see Sec. III C).

(B) The optimal r_{HH} distance of 1.42 Å for the MP2 calculations is much shorter (by 0.41 Å) than for the SCF calculations. A similar correlation-dependence of the anion-molecule distance was observed for H_3^- .³⁵ Cremer and Kraka did not notice this effect (their $r_{\text{HH}}^{\text{SCF}} = 1.51$ Å) because, at the SCF level, they used a basis set without any diffuse functions, 6-31G*, which we found to give a BSSE for H^- of ~ 20 kcal/mol. As a result, this basis is not, in our opinion, capable of accurate geometry optimization.

We went on to address the extent to which the above conclusions would be modified either by the correction for BSSE (in the gradient geometry optimization codes one

TABLE II. Optimized SCF and MP2 geometries of $\text{H}^- (\text{H}_2\text{O})$, "bent" and "bifurcated" (cf. Fig. 1). MP2 results without core correlation. Energies in Hartrees, distances in Å.

	SCF/A	MP2/A	MP2/C
Bent			
r_{OH}	0.9427	0.9665	0.9724
r'_{OH}	0.9687	1.0370	1.0368
r_{HH}	1.8318	1.4192	1.4315
θ_{HOH}	101.92°	99.21°	99.40°
θ_{HHO}	165.63°	172.90°	173.28°
E	SCF = - 76.566 004 MP2 = - 76.824 354 MP2 = - 76.798 266		
Bifurcated			
r_{OH}	0.9489	0.9768	
r'_{OH}	0.9489	0.9768	
r_{HH}	2.9179	2.6455	
θ_{HOH}	97.89°	92.37°	
	SCF = - 76.563 419 MP2 = - 76.818 517		

moves on the CP-uncorrected potential surface) or by allowing for higher-order electron correlation effects (i.e., by moving from MP2 to the MP4 level).

To address these questions, the most sensitive geometrical parameter, the r_{HH} distance, was varied. Both CP-corrected and uncorrected energies were calculated at the MP4/*A* level. The CP correction was found to slightly shorten r_{HH} distance whereas the MP4 treatment tended to slightly elongate r_{HH} relative to its MP2 value. Neither of the changes in r_{HH} exceeded 0.03 Å.

C. The interaction energy and its decomposition basis set effects

For the sake of convenience in the following discussion, the water molecule and the H^- ion will be denoted by "*W*" and "*H*", respectively. Furthermore, to distinguish between the two water molecules in $\text{H}^- (\text{H}_2\text{O})_2$ the subscripts "*a*" and "*b*" (e.g., W_a, W_b) will be used. For each of our basis sets, the magnitudes of the interaction energy and its various components, evaluated at the MP2 basis set *A* optimal geometry are presented in Tables III and IV. The three large basis sets *A*, *A**, and *B* provide, after application of the CP correction, interaction energies in the range from -16.2 to -16.9 kcal/mol.

TABLE III. The interaction energy and its components, for the $\text{H}^- (\text{H}_2\text{O})$ complex, obtained with different basis sets in the frozen core approximation. Energies in kcal/mol.

Term:	MP4/A // MP2/A			MP4/A* // MP2/A			MP4/B // MP2/A			MP4/C // MP2/C		
<i>i</i>	$\Delta E_{WH}^{(i)}$	$\delta_W^{(i)}$	$\delta_H^{(i)}$	$\Delta E_{WH}^{(i)}$	$\delta_W^{(i)}$	$\delta_H^{(i)}$	$\Delta E_{WH}^{(i)}$	$\delta_W^{(i)}$	$\delta_H^{(i)}$	$\Delta E_{WH}^{(i)}$	$\delta_W^{(i)}$	$\delta_H^{(i)}$
SCF	-10.52	-0.036	-0.053	-10.53	-0.114	-0.085	-10.21	-0.038	-0.029	-9.67	-0.166	-0.318
2	-7.23	-0.137	-0.850	-7.23	-0.331	-1.119	-6.96	-0.213	-0.492	-6.52	-0.401	-0.602
3	+2.15	+0.003	+0.153	+2.14	+0.023	+0.176	+2.23	+0.000	+0.282	+1.95	-0.002	+0.011
4	-1.23	-0.007	-0.034	-1.31	-0.028	+0.041	-1.26	-0.016	+0.081	-0.62	-0.025	+0.006
Sum	-16.83	-0.177	-0.784	-16.93	-0.450	-0.987	-16.21	-0.267	-0.158	-14.86	-0.594	-0.903
	(-17.79) ^a			(-18.37) ^a			(-16.64) ^a			(-16.36) ^a		

^a The value of the sum when CP-uncorrected.

^b The geometry of $\text{H}^- (\text{H}_2\text{O})$ was the one this system has in the $\text{H}^- (\text{H}_2\text{O})_2$ complex, cf. Table IX, i.e., slightly different from the MP2/*C* geometry. The difference is insignificant energetically, ~ 0.02 kcal/mol.

TABLE IV. Decomposition of the interaction energy for the $\text{H}^- (\text{H}_2\text{O})$ complex, obtained with basis B . The geometry of isolated water molecule was $\theta_{\text{HOH}} = 105.5^\circ$ and $r_{\text{OH}} = 0.964 \text{ \AA}$. Energies in kcal/mol, total energies, $E^{(i)}$, in Hartrees.

Term	$\Delta E_{WH}^{(i)}$	$\bar{\Delta E}_W^{(i)a}$	$\delta_W^{(i)}$	$\delta_H^{(i)}$	$E_W^{(i)a}$	$E_H^{(i)b}$	$E_{WH}^{(i)}$
SCF	-10.21	+5.34	-0.038	-0.029	-76.059 574	-0.487 787	-76.563 738
2	-6.96	-2.23	-0.213	-0.492	-0.229 585	-0.026 574	-0.268 383
3	+2.23	+0.50	+0.000	+0.282	-0.002 063	-0.007 600	-0.056 61
4-SD	-0.77	-0.18	+0.004	+0.071	-0.001 807	-0.002 494	-0.003 531
4-SDQ	-0.64	-0.34	+0.004	+0.081	-0.003 917	-0.002 695	-0.006 539
4-SDTQ	-1.26	-0.66	-0.016	+0.081	-0.010 937	-0.002 695	-0.015 526
Sum	-16.21	+2.94	-0.266	-0.158	-76.302 159	-0.524 655	-76.853 308

^a Calculated with the basis of water.^b Calculated with the basis of H^- .

In all cases BSSE is of the order of 1 kcal/mol and it is dominated by the BSSE in $\Delta E^{(2)}$, $\delta^{(2)}$. 1 kcal/mol is not large when compared either to the SCF or correlation contributions to the interaction energy. The smallest value of BSSE is obtained, as expected, for basis B : $\delta^{\text{SCF}} \approx 0.07$ kcal/mol and $\delta^{\text{MP4}} \approx 0.42$ kcal/mol. In this case $\delta^{(2)}$ is larger than the total BSSE (δ^{MP4}) but $\delta^{(3)}$ cancels part of $\delta^{(2)}$. Furthermore, the distribution of $\delta^{(i)}$ between $\delta_W^{(i)}$ and $\delta_H^{(i)}$ is fairly even. This is not the case for bases A and A^* where most of the BSSE is contained in the H^- . It is also important to remark that $\Delta E^{(4)}$ turned out to be insensitive to the addition of the polarization functions in basis A^* , although it produced a substantially larger δ . It should be kept in mind that we limited ourselves to only one f function—there is little doubt that our results for correlation are saturated. It has been recently shown that the role of higher polarization functions is much more important than it has been widely believed.^{39,40}

The basis labeled C was specifically designed to be used in our $\text{H}^- (\text{H}_2\text{O})_2$ calculations. Although it is smaller than bases A , A^* and B , it gives the geometry of $\text{H}^- (\text{H}_2\text{O})$ (cf. Table II) and energies (cf. Table III) fairly close to those obtained with the better bases. Only the result for $\Delta E_{WH}^{(4)}$ is in rather poor agreement with the larger bases.

1. Contributions to $\Delta E_{WH}^{(4)}$

To demonstrate the decomposition of $\Delta E_{WH}^{(4)}$, into its various parts, the results obtained with basis B , the one with the smallest BSSE, are shown in Table IV. $\text{H}^- (\text{H}_2\text{O})$ is a relatively strong complex and is strongly bound already at the SCF level: the SCF interaction energy calculated at the “bent” MP2/ A geometry with B basis amounts to 10.2 kcal/mol. In fact, the interaction energy between the deformed water and H^- , $\bar{\Delta E}_{WH}$, is larger (~ 15.5 kcal/mol) but the deformation of the water molecule brings about 5.3 kcal/mol of a destabilizing contribution (see Table IV). Allowing for electron correlation affects the r_{HH} distance considerably and makes the potential more attractive by 6 kcal/mol at the MP2/ A geometry (i.e., constitutes 35% of the total interaction energy). The deformation, in contrast to the SCF case, enhances the interaction energy by 2.2 kcal/mol.

We find that the total correlation effect is well approximated by $\Delta E_{WH}^{(2)}$ alone (i.e., it gives 16% too much binding compared with the fourth-order result). We also find that

the series $\Delta E_{WH}^{(i)}$ seems to oscillate in sign with $\Delta E_{WH}^{(2)}$ attractive, $\Delta E_{WH}^{(3)}$ repulsive, and $\Delta E_{WH}^{(4)}$ attractive again. The individual energy corrections do not differ substantially among the A , A^* , and B bases, nor do the individual contributions to $\Delta E_{WH}^{(4)}$. The SDQ terms are attractive and yield half as much as the total $\Delta E_{WH}^{(4)}$, which also includes T terms. The total $\Delta E_{WH}^{(4)}$ amounts to a small but quantitatively significant contribution of 1.3 kcal/mol.

One should remember that the trends described above depend on the distance between H_2O and H^- and the remarks made above pertain to the equilibrium bent geometry. For large R , $\Delta E_{WH}^{(2)}$ gives a repulsive contribution due to the fact $\Delta E_{WH}^{(2)}$ is then determined by the charge-dipole interaction (recall that the HF dipole moment of H_2O is too large). At shorter distances, the attractive dispersion term, as well as the exchange terms, become important. Note that the equilibrium geometry of $\text{H}^- (\text{H}_2\text{O})$ cannot be predicted by considering long-range charge-dipole interaction. The asymptotically optimal “bifurcated” geometry gives only a local energy minimum; the minimum with the H^- nearer to one of the H atoms is lower in energy.

The harmonic vibrational frequencies of $\text{H}^- (\text{H}_2\text{O})$ calculated at the MP2 level are given in Table V, as are the frequencies of H_2O evaluated using this same basis at the MP2 level. One clearly identifies two of these frequencies of H_2O (the bend at $\sim 1650 \text{ cm}^{-1}$ and one OH stretch at $\sim 3800 \text{ cm}^{-1}$) in the $\text{H}^- (\text{H}_2\text{O})$ frequency unit. The other OH stretch at $\sim 2500 \text{ cm}^{-1}$ is perturbed strongly by the nearby H^- ion. The three low frequency modes correspond to interspecies vibrations which involve motion of H^- relative to H_2O .

TABLE V. Harmonic vibrational frequencies of H_2O and $\text{H}^- (\text{H}_2\text{O})$ (in cm^{-1}).

H_2O			$\text{H}^- (\text{H}_2\text{O})$	
mode	MP2/ A	experiment ^a	mode	MP2/ A
A_1	1631.7	1595	A'	532.2
A_1	3798.9	3657	A'	647.1
B_2	3924.3	3756	A''	1005.2
			A'	1656.9
			A'	2472.9
			A'	3823.6

^a From Ref. 48.

D. The energetics of the proton-transfer reaction

The complex $\text{H}^-(\text{H}_2\text{O})$ may be considered as a possible intermediate in a proton transfer reaction

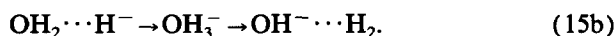


Reaction (15) is known to be fast and exothermic, $\Delta H_f^{298} = -10.1$ kcal/mol (Betowski *et al.*⁴¹). This reaction may be thought of as composed of three distinct stages (see also Fig. 2).

(i) Formation of the relatively strong $\text{H}^-(\text{H}_2\text{O})$ complex:



(ii) $\text{H}^-(\text{H}_2\text{O})$ passes through a transition state and a weak van der Waals complex $\text{OH}^-(\text{H}_2)$ is formed:



(iii) The $\text{OH}^- \cdots \text{H}_2$ complex dissociates into OH^- and H_2 :



The energies of the reactants and products in these reactions, calculated at the MP4 level and at the MP2/A geometries, are given in Table VII. The energy profile of reaction (15) is visualized in Fig. 2.

1. Formation of the $\text{H}^-(\text{H}_2\text{O})$ complex

The process of formation of the $\text{H}^-(\text{H}_2\text{O})$ complex, Eq. (15a), was investigated experimentally by Paulson and Henschman.² The enthalpy of this process was estimated in Ref. 2 to be

$$\Delta H_f^{298} = -17.3 \pm 1.2 \text{ kcal/mol.}$$

ΔH_f^{298} may also be calculated *ab initio* by allowing for the changes in translation, rotation, and vibration energies and in the number of modes, according to the formula⁴²

$$\Delta H^{298} = \Delta PV + \Delta E_e^0 + \Delta(\Delta E_e)^{298} + \Delta E_v^0 + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298}. \quad (16)$$

Particular terms are equal to

$$\Delta PV = -RT = -0.60 \text{ kcal/mol (one mole of gas is lost).}$$

$$\Delta E_e^0 = -16.2 \text{ to } -16.9 \text{ kcal/mol (present calculations, Table III).}$$

$$\Delta(\Delta E_e)^{298} \approx 0.$$

TABLE VI. The geometries of the transition state of H_3O^+ and the $\text{OH}^-(\text{H}_2)$ complex (cf. Fig. 1). Distances in Å, energies in Hartrees.

Transition state		$\text{OH}^-(\text{H}_2)$		
	MP2/A		SCF/A	MP2/A
r_{OH}	0.9702	r_{OH}	0.9449	0.9701
r'_{OH}	1.2755	r'_{OH}	2.0731	1.9703
r_{HH}	0.9949	r_{HH}	0.7555	0.7628
θ_{HOH}	98.94°	Energy	SCF = -76.549 418	MP2 = -76.825 351
θ_{HHO}	178.69°			
Energy	MP2 = -76.821 700			

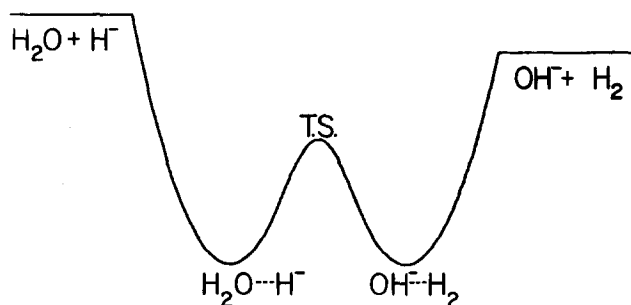


FIG. 2. Energy profile of reaction (15).

$$\Delta E_v^0 = \frac{1}{2} \left[\sum_{\text{H}_2\text{O}} \omega_i - \sum_{\text{H}_2\text{O}^-} \omega_i \right] = 2.23 \text{ kcal/mol}$$

(treating as harmonic the frequencies in Table V).

$\Delta(\Delta E_v)^{298} \approx 0.23$ kcal/mol. (This is the temperature correction to the vibrational term.)

$\Delta E_r \approx 0$ (classical approximation).

$\Delta E_{tr} = -3/2 RT = -0.89$ kcal/mol (3 degrees of freedom of translations are lost).

The addition of these contributions yields

$$\Delta H^{298} = \Delta E_e^0 - 0.97 \text{ kcal/mol.}$$

If we use the lowest and the highest value of ΔE_e^0 from Table III as (but neglecting the result with the small basis C), we obtain the following estimate of ΔH_f^{298}

$$\Delta H_f^{298} = -15.2 \text{ to } -16.0 \text{ kcal/mol.}$$

The above result lies just above the lower bound of the experimental assessment, -16.1 kcal/mol.

2. Transition state

The geometry of the transition state is shown in Fig. 1 (cf. Cremer and Kraka⁸), the geometrical parameters obtained at the MP2 level with basis A are in Table VI and the energies in Table VI (at the MP2 level) and in Table VII (at the MP4 level). We can also see in Table VII that the transition state presents a barrier of ~ 2.5 kcal/mol for the reaction given by Eq. (15b). Note, however, that MPPT may be expected to be well converged only at equilibrium geometries.¹⁸

TABLE VII. The absolute and relative energies of the components of Eq. (15). The energies were calculated at the MP4//MP2/A level (cf. Table II and VI).

Species	Configuration	Energy (H) MP4//MP2/A	Energy CP- Corrected ^b (H)	Energy difference ^a (kcal/mol)	Energy difference ^a CP-corrected (kcal/mol)
$\text{H}_2\text{O} + \text{H}^-$	isolated	-76.817 514			
$\text{H}_2\text{O} \cdots \text{H}^-$	bent	-76.845 861	-76.844 33	17.8	16.8
H_3O^-	transition state	-76.841 801		2.5	
$\text{OH}^- \cdots \text{H}_2$	linear	-76.846 000	-76.844 04	2.6	
$\text{OH}^- + \text{H}_2$	isolated	-76.837 646		5.2	4.0

^a Absolute energy differences between the neighbor rows.^b Obtained by subtracting δ from the total energy of the complex.

3. van der Waals complex $\text{OH}^-(\text{H}_2)$ and its dissociation into $\text{OH}^- + \text{H}_2$

The geometry of the $\text{OH}^-(\text{H}_2)$ complex (linear) is shown in Fig. 1; the geometrical parameters obtained at the MP2 level with basis A are in Table VI and the related energies in Table VIII. The $\text{OH}^-(\text{H}_2)$ complex turns out to be stable by 4.0 kcal/mol with respect to the products $\text{OH}^- + \text{H}_2$ (cf. Table VII).

However, the results for the $\text{OH}^- \cdots \text{H}_2$ complex are expected to be less accurate than those for $\text{H}^- \cdots \text{H}_2\text{O}$. In Table VIII the decomposition of the interaction energy in $\text{OH}^- \cdots \text{H}_2$ is shown. The complex is fairly weak and the interaction energy is dominated by ΔE_{SCF} . The BSSE is, however, relatively more important than for the stronger $\text{H}^- \cdots \text{H}_2\text{O}$ complex; in fact, it exceeds the correlation contribution to the interaction energy. The convergence of the $\Delta E^{(i)}$ series does not appear to be excellent either: $|\Delta E^{(3)}| > |\Delta E^{(2)}|$ and $\Delta E^{(3)} \approx -\Delta E^{(4)}$. In fact, the problems with convergence of the MPPT series are also present for the monomer OH^- where, an example, $E^{(4)} \approx -2E^{(3)}$ (cf. Table VIII).

4. The energetics of the total process $\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$

On the basis of the results of Table VII one can conclude the following. The difference between the electronic energies of the $\text{H}^- + \text{H}_2\text{O}$ reactants and the $\text{OH}^- + \text{H}_2$ products is

12.6 kcal/mol. The difference in the enthalpies, ΔH_f^{298} calculated according to Eq. (16) amounts to 14.4 kcal/mol. The individual terms in Eq. (16) are:

$$\begin{aligned}\Delta PV &= 0, \\ \Delta E_e^0 &= -12.6 \text{ kcal/mol}, \\ \Delta(\Delta E_e)^{298} &\approx 0, \\ \Delta E_v^0 &= -2.09 \text{ kcal/mol}, \\ \Delta(\Delta E_v)^{298} &\approx 0, \\ \Delta E_r^{298} &= \frac{1}{2}RT = 0.30 \text{ kcal/mol}, \\ \Delta E_f^{298} &= 0.\end{aligned}$$

On adding up one obtains $\Delta H_f^{298} = -14.4$ kcal/mol. The 4.3 kcal/mol difference between this result and the experimental one (-10.1 kcal/mol⁴¹) should be attributed to different accuracy of *ab initio* evaluations of the reactant and product energies: in particular the basis set is not equally good for H_2O and OH^- and MP4 does not recover the same portion of the correlation energy either.¹

The fact that the $\text{OH}^- + \text{H}_2$ energy should be lowered with respect to $\text{H}^- + \text{H}_2\text{O}$ energy by ~ 4 kcal/mol has to be taken into consideration when comparing the *ab initio* calculated energies of the $\text{H}^- \cdots \text{H}_2\text{O}$ and $\text{OH}^- \cdots \text{H}_2$ complexes. According to Table VII, both the complexes have the same electronic energy, within the error bars ± 0.2 kcal/mol (the result depends on whether we remove the BSE effect from

TABLE VIII. The decomposition of the interaction energy $\Delta E_{\text{MP}}(4)$ obtained at the MP4//MP2/A level for the linear $\text{OH}^-(\text{H}_2)$ complex. $\Delta E^{(i)}$ and $\delta^{(i)}$ in kcal/mol, total energies E in Hartrees.

Term	$\Delta E_{\text{OH}^-(\text{H}_2)}^{(i)}$	$\delta_{\text{OH}^-}^{(i)}$	$\delta_{\text{H}_2}^{(i)}$	$E_{\text{OH}^-}^{(i)a}$	$E_{\text{H}_2}^{(i)b}$	$E_{\text{OH}^-(\text{H}_2)}^{(i)}$
SCF	-3.753	-0.094	-0.242	-75.410 247	-1.131 765	-76.548 614
2	-0.301	-0.316	-0.255	-0.247 101	-0.027 947	-0.276 737
3	-0.531	+0.014	-0.055	+0.011 553	-0.005 986	+0.004 669
4	+0.576	-0.026	-0.011	-0.024 619	-0.001 533	-0.025 316
Sum	-4.01	-0.422	-0.563	-75.670 414	-1.167 232	-76.845 997

^a $r_{\text{OH}} = 0.971$ Å.^b $r_{\text{HH}} = 0.734$ Å.

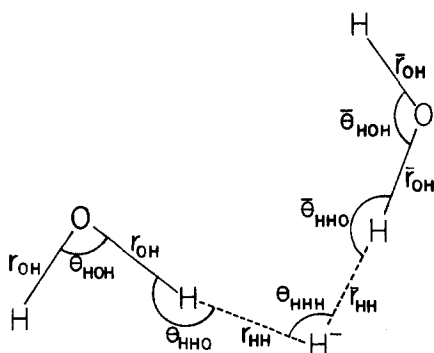


FIG. 3. Geometry of the $\text{H}^- (\text{H}_2\text{O})_2$ complex.

monomer energies or not). However, once realized that the energy of $\text{OH}^- \cdots \text{H}_2$ should be raised by ~ 4 kcal/mol with respect to $\text{H}^- \cdots \text{H}_2\text{O}$, one concludes that $\text{OH}^- \cdots \text{H}_2$ complex should be ~ 4 kcal/mol less stable than the $\text{H}^- \cdots \text{H}_2\text{O}$ complex.

V. $\text{H}^- (\text{H}_2\text{O})_2$

A. Geometry optimization

In all of our calculations on $\text{H}^- (\text{H}_2\text{O})_2$, basis *C* was used. The optimal geometry of $\text{H}^- (\text{H}_2\text{O})_2$ is shown in Fig. 3. It is likely that this geometry, with both waters aggregated around the H^- , is energetically best because the $\text{H}^- \cdots \text{H}_2\text{O}$ interaction is much stronger than the $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ interaction. Our geometry optimization was carried out in two steps. First, the geometries of the "overlapping" $\text{H}^- (\text{H}_2\text{O})$ subunits were fixed at the MP2/*C* geometry shown in Table II, and only the θ_{HHH} (see Fig. 3) angle was varied. The minimum along this geometry variation path was found at 95° . However, between 95° and 180° the energy rose only by 0.4 kcal/mol; at 160° an extremely broad local maximum was also found. For $\theta_{\text{HHH}} < 95^\circ$ the energy rises rapidly; at 70° and 50° it is 2 and 44 kcal/mol, respectively, above the 95° minimum. For $\theta_{\text{HHH}} > 95^\circ$ (i.e., in the "flat region") we checked the geometry with one $\text{H}^- (\text{H}_2\text{O})$ unit rotated around r_{HH} by 180° . At $\theta_{\text{HHH}} = 100^\circ$ and 160° the energy increased by 1.0 and 0.4 kcal/mol, respectively.

In the second step of our optimization, we varied, at $\theta_{\text{HHH}} = 95^\circ$, the geometries of the $\text{H}^- (\text{H}_2\text{O})$ subunits, but keeping their geometries identical. The resulting geometries are shown in Table IX and compared to the MP2/*C* geometry of $\text{H}^- (\text{H}_2\text{O})$. One can see that only the r_{HH} distance was

appreciably affected; it became longer by 0.03 Å compared to the $\text{H}^- (\text{H}_2\text{O})$ case. Allowing, in addition, for independent variations of the r_{HH} and \bar{r}_{HH} distances shortened one distance by 0.016 Å, elongated the other by 0.016 Å, and changed the energy by 0.01 kcal/mol. It was also found that opening the θ_{HHH} to 180° while keeping $\bar{\theta}_{\text{HHH}}$ as in Table IX yielded extra stabilization of ~ 0.1 kcal/mol.

B. Interaction energy in the $\text{H}^- (\text{H}_2\text{O})_2$ complex

The values of the one-, two-, and three-body energy terms for $\text{H}^- (\text{H}_2\text{O})_2$, at the MP2/*C* geometry, are listed in Table X. The $DE_{w_a w_b}^{(1)}$ terms are not shown as they turned out to be negligible. The values of $\Delta E_{H w_a w_b \rightarrow H w_a}$ and $\Delta E_{H w_a \rightarrow H}$ are also given. One can see that although the three-body effect $\tilde{\Delta E}_{w_a w_b H}$ brings about 0.5 kcal/mol of attractive contribution, the water–water interaction is repulsive by +1.2 kcal/mol and the overall effect of adding the second water ($\Delta E_{H w_a w_b \rightarrow H w_a}$) is slightly smaller than that of adding the first one ($\Delta E_{H w_a \rightarrow H}$). This result is qualitatively in agreement with the experimental measurements of the related enthalpies for other atomic anions–water complexes (Kearle *et al.*⁴³). It is important to stress that if one used the CP-uncorrected results to evaluate $\Delta E_{H w_a w_b \rightarrow H w_a}$ one would obtain the opposite result—additional stabilization of the $\text{H} (\text{H}_2\text{O})$ subunit by adding the second water. Thus, CP corrections are of essential importance. It is also useful to note that basis *C* is not as good as *A* and *B* and that the water–water term $\tilde{\Delta E}_{w_a w_b}$ is small and strongly affected by BSSE. As to the convergence of the $\Delta E_{w_a w_b}^{(i)}$ corrections, $\tilde{\Delta E}_{w_a w_b}^{(3)}$ is smaller than $\tilde{\Delta E}_{w_a w_b}^{(4)}$ at the geometry of Fig. 3, but fortunately both the corrections are very small compared with $\Delta E_{w_a w_b}^{(4)}$.

VI. CONCLUSIONS

It has already been established by Cramer and Kraka⁸ and Squires⁷ that the equilibrium geometry of $\text{H}^- (\text{H}_2\text{O})$ is not "bifurcated," as predicted by the electrostatic model of intermolecular interactions, but "bent" (Fig. 1). The present work confirmed such a geometry.

An important new finding is that electron-correlation effects are very important. They cause shortening of the equilibrium r_{HH} distance by a significant amount (0.4 Å) and provide one-third of the total interaction energy at the equilibrium distance. It is worthwhile to note that analogous results were found for the $\text{H}^- (\text{H}_2)$ complex in our laboratory.³⁵ The conclusion is that for anion–molecule complexes, one must not restrict oneself to the optimization of geometry at the SCF level, as has often been done,^{7,45–47} but one must allow for electron-correlation effects at least at the MP2 level. It was found that moving to the MP4 level of theory does not have a pronounced effect on the geometry.

An adequate choice of basis sets, in particular one which includes diffuse and polarization functions, is also very important. Although it has been recognized for some time that diffuse functions are absolutely necessary in the calculations of anion and van der Waals complexes,³⁷ it is fairly common to optimize the geometry at the SCF level with basis 6-31G* or worse^{8,45–47} and to then do, at this geometry, single-point

TABLE IX. The MP2/*C* geometry of $\text{H}^- (\text{H}_2\text{O})$ and $\text{H}^- (\text{H}_2\text{O})_2$. Distances in Å.

	$\text{H}^- (\text{H}_2\text{O})$	$\text{H}^- (\text{H}_2\text{O})_2$
$r_{\text{OH}} = \bar{r}_{\text{OH}} =$	0.9724	0.9720
$r'_{\text{OH}} = \bar{r}'_{\text{OH}} =$	1.0368	1.0258
$r_{\text{HH}} = \bar{r}_{\text{HH}} =$	1.4315	1.4597
$\theta_{\text{HOH}} = \bar{\theta}_{\text{HOH}} =$	99.40°	100.16°
$\theta_{\text{HHO}} = \bar{\theta}_{\text{HHO}} =$	173.28°	175.20°
$\theta_{\text{HHH}} =$...	95°

TABLE X. The interaction energy and its components for $\text{H}^-(\text{H}_2\text{O})_2$ obtained at the MP4/C//MP2/C level. Energies in kcal/mol.

i	$\tilde{\Delta E}_W^{(i)}$	$\tilde{\Delta E}_{W_a H}^{(i)}$	$\tilde{\Delta E}_{W_b H}^{(i)}$	$\tilde{\Delta E}_{WH}^{(i)\text{uncorr. a}}$	$\tilde{\Delta E}_{W_a W_b}^{(i)}$	$\tilde{\Delta E}_{W_a W_b}^{(i)\text{uncorr. a}}$
SCF	+ 3.776	− 13.605	− 13.636	− 13.930	+ 1.888	+ 1.830
2	− 2.315	− 4.167	− 4.201	− 5.211	− 0.585	− 1.041
3	+ 0.381	+ 1.540	+ 1.540	+ 1.565	− 0.027	− 0.044
4	− 0.542	− 0.117	− 0.117	− 0.093	− 0.140	− 0.182
Sum	+ 1.301	− 16.349	− 16.415	− 17.669	+ 1.136	+ 0.563

i	$\tilde{\Delta E}_{W_a W_b H}^{(i)}$	$\tilde{\Delta E}_{W_a W_b H}^{(i)\text{uncorr. a}}$	$\Delta E_{W_a W_b H}^{(i)}$	$\Delta E_{HW_a-H}^{(i)}$	$\Delta E_{HW_a W_b-HW_a}^{(i)}$
SCF	− 1.473	− 1.839	− 19.274	− 9.829	− 9.445
2	+ 1.316	+ 1.533	− 12.267	− 6.482	− 5.785
3	− 0.400	− 0.404	+ 3.415	+ 1.921	+ 1.494
4	+ 0.030	− 0.048	− 1.428	− 0.659	− 0.769
Sum	− 0.528	− 0.758	− 29.554	− 15.048	− 14.506

^a CP-uncorrected result.

calculations with better basis sets and at the post-Hartree-Fock level.^{7,45-47} However, we have found in the case of $\text{H}^-(\text{H}_2\text{O})$ that using the 6-31G* basis at the SCF level leads to a BSSE of 20 kcal/mol which is more than the interaction energy itself. Since the analytical energy gradients method uses the CP-uncorrected energy surface, one can, thus, expect substantial deformation of the optimized geometry with such a poor basis. The SCF/6-31G* value of r_{HH} obtained by Cremer and Kraka is too short by ~ 0.3 Å with respect to our extended basis set calculations. Accidentally, this basis set effect fortuitously cancels the electron-correlation effect and the equilibrium distance r_{HH} evaluated at the SCF/6-31G* level is only slightly longer (0.03 Å), that calculated at the MP2/6-31 + + G** level.⁸

The above discussion and our study demonstrate how important it is to choose a proper basis set for complexes with anions. The BSSE should be kept small if one uses energy gradient methods. The value of the BSSE should then be controlled and the interaction energies should be obtained by means of the CP method. If the subsystems are deformed in the complex with respect to their isolated geometries, the deformation effect may be calculated separately and added to the value of the interaction energy between these deformed systems by means of the CP method as described in this paper. It is worthwhile to note that the BSSE problem is expected to be more serious for weaker complexes such as $\text{H}^-(\text{NH}_3)$ and $\text{H}^-(\text{CH}_4)$. We estimated the value of the enthalpy of formation ΔH_f^{298} of $\text{H}^-(\text{H}_2\text{O})$ to be in the range - 15.2 to - 16.0 kcal/mol compared with the experimental value of 17.3 ± 1.2 kcal/mol.² Our ΔH_f^{298} may be slightly too small because of basis set unsaturation, in particular in the polarization function set. There is also the question of the quality of the MP4 level since we found the perturbation series to be convergent in an oscillating way. On the other hand, the experimental results is not very precise either.

We found it difficult to obtain accurate results for ΔH^{298} for the proton-transfer reaction, Eq. (15); our $\Delta H^{258} = - 14.4$ kcal/mol does not compare well with the experimental value, - 10.1 kcal/mol.⁴¹ An accurate ΔH^{298} seems to be a difficult calculation since it is 500 times smaller than the energies of the reactants or products in Eq. (15)

and the accuracy of reproducing these energies, in particular those of H_2O and OH^- , with our basis sets and the MP4 method may differ enough to bring about nontrivial discrepancies.

Our calculations of the $\text{H}^-(\text{H}_2\text{O})_2$ complex employed a smaller basis set which was, however, shown to give reliable results for $\text{H}^-(\text{H}_2\text{O})$. The two most important observations for this system are:

- (1) The potential surface is very flat with respect to the θ_{HHH} angle and along any distortions which do not modify the geometry of $\text{H}^-(\text{H}_2\text{O})$ subunits.
- (2) The energy change due to the loss of the first water is 0.5 kcal/mol smaller than the energy change due to the loss of the second water. This is in qualitative agreement with the results of experiments with halogen anions and water molecules.⁴³ It is worthwhile to note that just the opposite result is obtained if the CP method is not used.

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