

# A first principles study of the acetylene–water interaction

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We present an extensive study of the stationary points on the acetylene–water (AW) ground-state potential energy surface (PES) aimed in establishing accurate energetics for the two different bonding scenarios that are considered. Those include arrangements in which water acts either as a proton acceptor from one of the acetylene hydrogen atoms or a proton donor to the triple bond. We used a hierarchy of theoretical methods to account for electron correlation [MP2 (second-order Moller–Plesset), MP4 (fourth-order Moller–Plesset), and CCSD(T) (coupled-cluster single double triple)] coupled with a series of increasing size augmented correlation consistent basis sets (aug-cc-pVnZ,  $n=2,3,4$ ). We furthermore examined the effect of corrections due to basis set superposition error (BSSE). We found that those have a large effect in altering the qualitative features of the PES of the complex. They are responsible for producing a structure of higher ( $C_{2v}$ ) symmetry for the global minimum. Zero-point energy (ZPE) corrections were found to increase the stability of the  $C_{2v}$  arrangement. For the global (water acceptor) minimum of  $C_{2v}$  symmetry our best estimates are  $\Delta E_e = -2.87$  kcal/mol ( $\Delta E_0 = -2.04$  kcal/mol) and a van der Waals distance of  $R_e = 2.190$  Å. The water donor arrangement lies 0.3 kcal/mol (0.5 kcal/mol including ZPE corrections) above the global minimum. The barrier for its isomerization to the global minimum is  $E_e = 0.18$  kcal/mol; however, inclusion of BSSE- and ZPE-corrections destabilize the water donor arrangement suggesting that it can readily convert to the global minimum. We therefore conclude that there exists only one minimum on the PES in accordance with previous experimental observations. To this end, vibrational averaging and to a lesser extend proper description of intermolecular interactions (BSSE) were found to have a large effect in altering the qualitative features of the ground-state PES of the acetylene–water complex. © 2000 American Institute of Physics. [S0021-9606(00)30214-8]

## I. INTRODUCTION

Hydrophobic interactions play an important role in many chemical and biochemical systems.<sup>1,2</sup> Notwithstanding the vagueness entailed in the term “hydrophobic” (fear of water), and all associated phenomena related to hydrophobicity, there is little doubt that this concept is associated with weak (van der Waals or hydrogen bonding) interactions between polar and nonpolar systems. In particular, interactions of the C–H···X type, where X is an electronegative moiety, have recently drawn discussion regarding not only the strength, but also the nature of such interactions, i.e., whether they are van der Waals or “genuine” hydrogen bonds.<sup>3</sup>

In this study we attempt a molecular level understanding of the microhydration pattern of acetylene (A) by examining the salient features of the acetylene–water (AW) cluster potential energy surface (PES). Our goal is to derive an accurate estimate of the strength of the A···W interaction and characterize the stationary points on the PES that correspond to different bonding scenarios. Subsequent studies will focus on the structures of the larger  $AW_n$  clusters ( $n=2-4$ ) as a

means of probing the perturbation of the water hydrogen bonding network due to the presence of the host molecule, A. These results can serve as benchmarks in the evaluation–parametrization of interaction potentials used to study aqueous solvation of model hydrocarbons.

Intuitively, one can think of two attractive modes of interaction that differ with respect to the orientation of W with respect to A. The first one corresponds to the water molecule acting as the proton acceptor from one of the acetylene H atoms ( $Y$ -,  $YY$ -structures), the other one with the water molecule acting as the (single or double) proton donor to the  $\pi$ -electron cloud of A ( $T$ -,  $TT$ -structures). In the previous notation, single letter attributes ( $Y$ ,  $T$ ) correspond to lower ( $C_s$ ) whereas double letter attributes ( $YY$ ,  $TT$ ) indicate structures of higher ( $C_{2v}$ ) symmetry. These (assumed) minima should be connected via a transition state ( $YT$ -structure). The relevant stationary points of the cluster PES pertaining to the previous discussion are pictorially shown in Fig. 1. In what follows we choose to refer to the AW dimer as a van der Waals rather than a hydrogen bonded system, due to the encompassing generality of the former term as compared to the latter.

Previous *ab initio* calculations on the AW complex are

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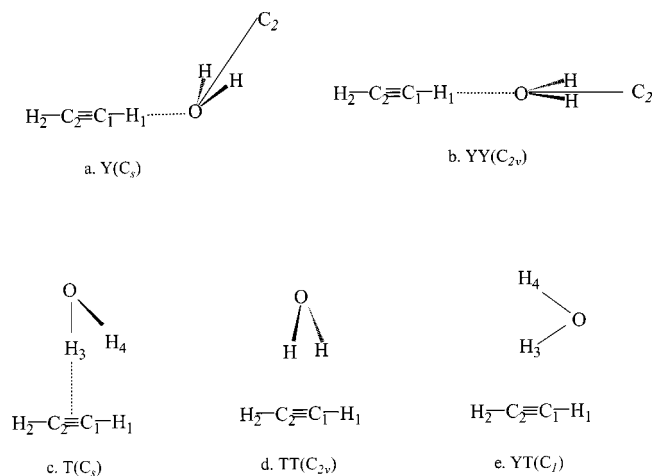


FIG. 1. Stationary points on the (AW) PES. (a) *Y*-minimum,  $C_s$ -symmetry (b) *YY*-t.s.,  $C_{2v}$ -symmetry (c) *T*-minimum,  $C_s$ -symmetry (d) *TT*-t.s.,  $C_{2v}$ -symmetry (e) *YT*-t.s.,  $C_1$ -symmetry.

summarized in the first part of Table I. The earliest calculation by Del Bene<sup>4</sup> examined only the *T*-minimum at the STO-3G/Hartree–Fock (HF) level, obtaining an equilibrium energy difference  $\Delta E_e (= E_{\text{AW}} - E_{\text{A}} - E_{\text{W}})$  of  $-3.5$  kcal/mol. A subsequent study by Frisch *et al.*<sup>5</sup> reported the *T*- and *Y*-minimum, and the *YT*-transition state at the Møller–Plesset fourth-order perturbation theory level using optimal HF ge-

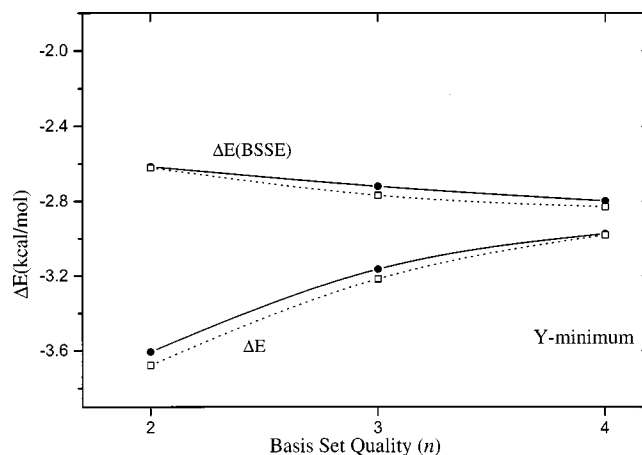


FIG. 2. Variation of the energy difference  $\Delta E_e$  (uncorrected and BSSE-corrected) for the *Y*-minimum with basis set size at the MP2 (solid circles) and MP4 (open squares) levels.

ometries (MP4SDQ/6-31G\*\*//HF/6-31G\*). Dykstra<sup>6</sup> has examined both *Y*- and *T*-minima using the electrically based molecular mechanics of clusters (MMC) approach (note that the captions for Figs. 2 and 3 are interchanged in this reference). The rest of the previous studies<sup>7–13</sup> have mainly examined the *Y*-minimum, although two of them also reported the highly symmetric *YY*-configuration.<sup>7,9</sup> Through all those previous papers (cf. Table I) the basis sets used range from

TABLE I. Previous theoretical and experimental results for the AW complex. Geometries (distances in Å, angles in degrees), total energies (hartrees), and energy differences  $\Delta E_e$  (kcal/mol). Subscripts “0” and “e” denote energy differences with and without zero-point corrections. BSSE-corrected numbers are shown in parentheses.

Method/basis set	Ref.	Config. <sup>a</sup>	$R_1^b/R_2^c$	$\phi_1^d/\phi_2^e$	$E_e$	$\Delta E_e$	$\Delta E_o$
Theory							
HF/STO-3G	4	<i>T</i>	3.63		...	-3.5	
HF/STO-3G	7	<i>Y</i>	2.940		-150.827 70	-3.49	
		<i>YY</i>	2.966		-150.827 18	-3.16	
MP4SDQ/6-31G**//HF/6-31G*	5	<i>Y</i>	3.320	126.2/132.4	-153.329 77	-3.0	
		<i>T</i>	3.556	165.4	-153.327 51	-1.6	
		<i>YT</i>	3.491	102.4	-153.327 49	-1.6	
MP2/6-31+G**	8	<i>Y</i>	2.202	147.35	-153.397 448	-3.25	-2.15
MP2/D95++ (dp)	9	<i>Y</i>	2.188/3.262	153.0/154.2	-153.390 264	-3.95 (-2.68)	-2.78 (-1.51)
		<i>YY</i>	2.191/3.264		-153.390 232	-3.93 (-2.73)	-2.98 (-1.78)
MP2/aug-cc-pVTZ//MP2/6-31++G(2d2p)	11	<i>Y</i>	3.282	146.2/146.9	-153.499 310	-3.13 (-2.77)	
DFT S-LYP//MP2/6-31++G(2d2p)		<i>Y</i>	2.939	172.1/172.2	-151.782 208	-5.44 (-5.40)	
DFT B-null//MP2/6-31++G(2d2p)		<i>Y</i>	3.759	172.2/172.0	-152.999 331	-0.29	
DFT B-VWN//MP2/6-31++G(2d2p)		<i>Y</i>	3.527	172.0/172.1	-155.008 546	-1.07	
MP2/D95++ (dp)	12	<i>Y</i>	2.196	123.9/123.0	-153.345 998	-3.93	-2.75
BSSE curve		<i>Y</i>	2.285	127.2	-153.343 968		
MMC	6	<i>Y</i>	3.898 <sup>f</sup>	93		-3.12	-2.06
		<i>YY</i>	4.062 <sup>f</sup>			-3.37	
		<i>T</i>	3.331 <sup>f</sup>			-3.42	-2.12
Experiment							
IR spectrum in Ar matrix	14	<i>Y</i>				-2 to -3 <sup>g</sup>	
microwave spectroscopy	15	<i>Y</i>	2.229				
<i>n</i> -IR, optothermal detection	8	<i>Y</i>					

<sup>a</sup>See Fig. 1.

<sup>b</sup>The van der Waals distances  $\text{CH}\equiv\text{CH}\cdots\text{OH}_2$  (*Y*) and  $\text{HOH}$ -middle of  $\text{C}\equiv\text{C}$  (*T*).

<sup>c</sup>The  $\text{C}_1\cdots\text{O}$  distance (*Y, T, YT*).

<sup>d</sup>The angle between the  $\text{H}_2\text{O}(\text{C}_2)$  and  $\text{C}\equiv\text{C}$  axis (*Y*), the angle  $\text{O}-\text{H}$ -middle of  $\text{C}\equiv\text{C}$  (*T*).

<sup>e</sup>The angle between the  $\text{H}_2\text{O}(\text{C}_2)$  and  $\text{C}-\text{O}$  axes (*Y*), the  $\text{C}\equiv\text{C}-\text{O}$  angle (*YT*).

<sup>f</sup>The distance between the centers of mass of the two fragments, A and W.

<sup>g</sup>Estimate for  $\Delta H_f$ .

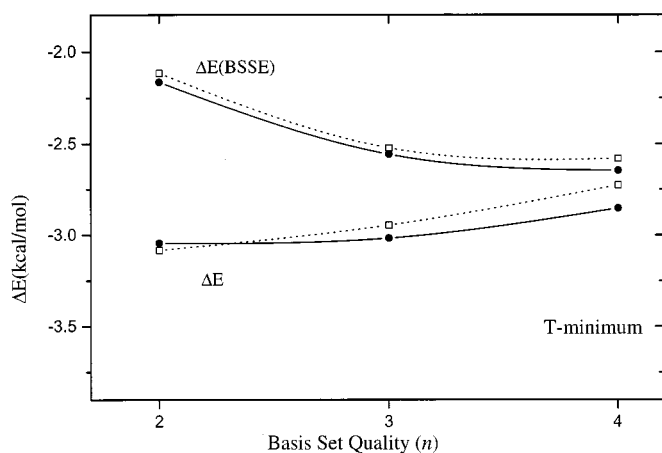


FIG. 3. Variation of the energy difference  $\Delta E_e$  (uncorrected and BSSE-corrected) for the *T*-minimum with basis set size at the MP2 (solid circles) and MP4 (open squares) levels.

minimal STO-3G (Refs. 4 and 7) to triple zeta+diffuse functions<sup>11</sup> and the level of electron correlation was extended up to second order in the perturbation expansion (MP2). Only the work of Frisch *et al.*<sup>5</sup> employed single point MP4SDQ energies but at the HF optimal geometries. Some density functional (DFT) calculations have also been previously reported but with rather dubious findings, as evidenced from the reported diverging results.

The second part of Table I condenses the results of previous experimental work for the AW system.<sup>8,14,15</sup> Engdahl and Nelander<sup>14</sup> have recorded the infrared (IR) spectra of argon matrices containing W and A and, based on the strongly red-shifted CH-stretching, the blue-shifted CH-deformation fundamentals of the complex and the small shifts in the water vibrations, have concluded that A forms a hydrogen bond with the oxygen atom of W. They have furthermore suggested a range of  $-2$  to  $-3$  kcal/mol for  $\Delta H_f$  based on the magnitude of the CH shift. Peterson and Klemperer<sup>15</sup> measured the radio frequency and microwave spectra of various isotopically substituted AW species and obtained rotational constants and dipole moments. Their analysis is consistent with an *effectively planar* geometry (*YY*-structure in Fig. 1) having all three heavy atoms in a collinear arrangement. A fit to the measured rotational constants produced a (vibrationally averaged) distance of 2.229 Å between the acetylene hydrogen and the water oxygen atoms. They also pointed out that vibrational averaging forbade the precise determination of the equilibrium structure as to whether there exists an inversion barrier at the planar configuration and the equilibrium structure has the water tilted out of the plane (*Y*-structure of Fig. 1). However, since the measured dipole moment increased upon deuteration, the barrier, if it exists, does not support a vibrational level within the double potential well.<sup>15</sup> This issue was revisited in a subsequent joint experimental-theoretical study by Miller and co-workers<sup>8</sup> who recorded near-infrared spectra in the 3 μm region and reported *ab initio* MP2 results with several basis sets of double zeta quality at the MP2 level of theory for the complex. These calculations confirmed that the complex undergoes large amplitude motions from its nonplanar

equilibrium geometry, therefore, effectively having a quasi-planar structure since the zero-point energy is larger than the height of the barrier.

The analysis of the data during all previous experimental studies suggests that only the *Y*-structure (cf. Fig. 1) was observed, a fact that implies that it is the global minimum. From the experiments no information could be deduced as to the nature of the *T*-structure configuration, i.e., whether it is a local minimum on the PES. Simple models, such as the one proposed by Buckingham and Fowler,<sup>16</sup> produce results for the two structures that are much closer in energy than the energy difference of 1.6 kcal/mol obtained from intermolecular perturbation theory.<sup>13</sup> A quantitative determination of the strength of the interaction in the *Y*- and *T*-arrangements is important in assessing the relative stability between families of stable configurations in clusters of A with more than one water molecules. For the larger clusters there is competition between the formation of gas phase-like cyclic water networks that attach to A and other networks which incorporate part of the host molecule (A) via *T*-like arrangements. Furthermore, an accurate number for the binding energy will also yield the minimum requirements as regards the theoretical treatment needed for the accurate description of the clusters of A with more than one water molecule, presented in a forthcoming study.

The previous discussion calls for a more accurate examination of the stationary points and energetics of the PES. In this study we present accurate structures and energetics for all five stationary points of Fig. 1. In Sec. II we outline the technical details of our calculations. The results are presented in Sec. III and final conclusions are drawn in Sec. IV.

## II. COMPUTATIONAL DETAILS

Throughout the present work we employed the family of augmented correlation consistent, aug-cc-pVnZ, basis sets of Dunning and co-workers;<sup>17</sup>  $n=2,3,4$  is codified with *D*, *T*, and *Q* for the double through quadruple sets, respectively, whereas aug- indicates diffuse functions, one extra diffuse set of functions added for every different angular momentum of the plain (non-augmented) basis. Hereafter, the basis set will be denoted as aug-cc-pVnZ or cc-pVnZ for the augmented and plain sets, respectively. All sets are generally contracted with the smaller (aug-cc-pVDZ) basis set  $\{(10s5p2d)_{C,O}/(5s2p)_H\} \rightarrow \{[4s3p2d]_{C,O}/[3s2p]_H\}$  containing 105 contracted spherical Gaussians, and the larger (aug-cc-pVQZ) set  $\{(13s7p4d3f2g)_{C,O}/(7s4p3d2f)_H\} \rightarrow \{[6s5p4d3f2g]_{C,O}/[5s4p3d2f]_H\}$  containing 424 contracted functions. Some calculations were also performed with the corresponding plain sets. Calculations were performed at the MP2, MP4, and CCSD(T) levels of theory in order to explore the effect of electron correlation on the computed structures and energetics.

The *Y*- and *T*-structures were fully optimized at the MP2/aug-cc-pVnZ ( $n=2-4$ ), MP4/aug-cc-pVnZ ( $n=2-3$ ) and CCSD(T)/aug-cc-pVnZ ( $n=2-3$ ) levels of theory. Single point energy calculations with the largest (aug-cc-pVQZ) set used here were performed at the MP4 level at the corresponding optimal geometries with the aug-cc-pVTZ set. During all optimizations the root-mean-square

TABLE II. Optimal geometries (Å, degrees) and energies (hartree) of Acetylene and Water. Experimental numbers are also shown.

Method	C <sub>2</sub> H <sub>2</sub>			H <sub>2</sub> O		
	R <sub>C-C</sub>	R <sub>C-H</sub>	E	R <sub>O-H</sub>	φ	E
aug-cc-pVDZ						
MP2	1.2315	1.0752	-77.092 997	0.9659	103.87	-76.260 909
MP4	1.2328	1.0783	-77.121 390	0.9670	103.88	-76.274 512
CCSD(T)	1.2301	1.0787	-77.121 383	0.9665	103.94	-76.273 904
aug-cc-pVTZ						
MP2	1.2122	1.0617	-77.164 058	0.9614	104.11	-76.328 992
MP4	1.2141	1.0639	-77.193 864	0.9627	104.06	-76.343 678
CCSD(T)	1.2102	1.0640	-77.192 198	0.9616	104.18	-76.342 326
aug-cc-pVQZ						
MP2	1.2092	1.0614	-77.185 736	0.9589	104.27	-76.351 919
MP4	1.2109	1.0636	-77.213 031	0.9601	104.24	-76.365 085
CCSD(T)	1.2069	1.0636	-77.210 997	0.9590	104.37	-76.363 588
Exp <sup>a,b</sup>	1.2033	1.0605		0.9587(1)	103.89(6)	
Exp <sup>c</sup>				0.95748(2)	105.019(13)	
Exp <sup>d</sup>				0.9572(3)	104.52	

<sup>a</sup>Reference 25(a) (C<sub>2</sub>H<sub>2</sub>).<sup>b</sup>Reference 26 (H<sub>2</sub>O).<sup>c</sup>Reference 26(b).<sup>d</sup>Reference 26(c).

(rms) deviations of the energy gradient with respect to nuclear coordinates were <1 μh/bohr; this corresponds to a change in the total energy of ~0.01 μh or less. The planar configuration of C<sub>2v</sub> symmetry (YY-structure) was also fully optimized in all three levels of theory with the n=2,3 sets. Finally, the YT- and TT-structures were optimized at the MP2/aug-cc-pVnZ, n=2,3 levels of theory. Harmonic frequencies were computed for all the five stationary points at the MP2/aug-cc-pVnZ (n=2,3) levels.

The AW equilibrium energy difference ΔE<sub>e</sub>(AW) is computed as:

$$\Delta E_e(\text{AW}) = E_{\text{AW}}^{aw}(\text{AW}) - E_{\text{A}}^a(\text{A}) - E_{\text{W}}^w(\text{W}) \quad (1)$$

where E<sub>G</sub><sup>s</sup>(M) refers to the total energy of the molecule M at the geometry G computed with basis set s. Basis set superposition error<sup>18</sup> corrections are obviously of critical importance in van der Waals systems such as the one studied here.<sup>19,20</sup> For finite basis sets, ΔE<sub>e</sub> is corrected for basis set superposition error (BSSE), according to<sup>21</sup>

$$\Delta E_e(\text{BSSE-corrected}) = E_{\text{AW}}^{aw}(\text{AW}) - E_{\text{AW}}^{aw}(\text{A}) - E_{\text{AW}}^{aw}(\text{W}) + R_1 + R_2, \quad (2)$$

where

$$R_1 = E_{\text{AW}}^a(\text{A}) - E_{\text{A}}^a(\text{A}), \quad (3a)$$

$$R_2 = E_{\text{AW}}^w(\text{W}) - E_{\text{W}}^w(\text{W}), \quad (3b)$$

are the “deformation” terms reflecting the energy penalty associated with the change of the fragments in the cluster from their isolated geometries.

Complete basis set limit (CBS) energy values, ΔE<sub>CBS</sub>, are estimated using the formula<sup>22</sup>

$$\Delta E = \Delta E_{\text{CBS}} + B e^{-Cn}, \quad (4)$$

where n is the cardinal basis set number (n=2, 3, and 4), and B, C fitting constants.

All calculations were performed with the GAUSSIAN94 (Ref. 23a), GAUSSIAN98 (Ref. 23b) and the MOLPRO (Ref. 24) suite of codes.

### III. RESULTS AND DISCUSSION

#### A. Isolated fragments C<sub>2</sub>H<sub>2</sub> (A) and H<sub>2</sub>O (W)

The optimal geometries and minimum energies of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O calculated at the MP2, MP4, CCSD(T)/aug-cc-pVnZ, n=2,3,4, are listed in Table II. For comparison, experimental values<sup>25,26</sup> are also listed. The MP4 and/or CCSD(T)/aug-cc-pVQZ geometries are in very good agreement with experiment. The harmonic vibrational frequencies (cm<sup>-1</sup>) and zero-point energies (kcal/mol) of the fragments are listed in Table III.

TABLE III. MP2 harmonic vibrational frequencies (cm<sup>-1</sup>) and zero-point energies (kcal/mol) of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O.

	C <sub>2</sub> H <sub>2</sub>		H <sub>2</sub> O		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	
ω <sub>4</sub> (π <sub>g</sub> )	409	601	ω <sub>2</sub> (a <sub>1</sub> )	1622	1628
ω <sub>5</sub> (π <sub>u</sub> )	703	754	ω <sub>1</sub> (a <sub>1</sub> )	3803	3822
ω <sub>2</sub> (σ <sub>g</sub> <sup>+</sup> )	1946	1968	ω <sub>3</sub> (b <sub>2</sub> )	3938	3948
ω <sub>3</sub> (σ <sub>u</sub> <sup>+</sup> )	3431	3432			
ω <sub>1</sub> (σ <sub>g</sub> <sup>+</sup> )	3519	3534			
ZPE	15.90	16.65	ZPE	13.39	13.44



TABLE IV. Geometry (Å, Degrees) and rotational constants (RC in GHz) of the *Y*-minimum with different basis sets and methodologies.

	aug-cc-pVDZ			aug-cc-pVTZ			aug-cc-pVQZ		Exp <sup>a</sup>	Exp <sup>b</sup>
	MP2	MP4	CCSD(T)	MP2	MP4	CCSD(T)	MP2			
$R_{C-C}$	1.2325	1.2340	1.2312	1.2134	1.2154	1.2115	1.2106			
$R_{C1-H1}$	1.0801	1.0831	1.0833	1.0667	1.0687	1.0686	1.0667			
$R_{H2-C2}$	1.0747	1.0778	1.0781	1.0620	1.0643	1.0643	1.0613			
$\phi_{H2C2C1}$	179.97	179.94	179.95	179.94	180.00	179.98	179.94			
$\phi_{C2C1H1}$	179.97	179.95	179.90	179.92	179.99	179.96	179.91			
$\phi_{C2C1O}$	179.94	179.98	180.00	179.50	179.97	179.99	179.44			
$R_{H-O}$	0.9657	0.9667	0.9664	0.9617	0.9629	0.9618	0.9591			
$\phi_{H3OH4}$	104.27	104.22	104.28	104.46	104.44	104.55	104.70			
$R_{C1-O}$	3.2535	3.2582	3.2658	3.2544	3.2534	3.2581	3.2575			
$\delta_{C2C1OH3}^c$	83.22	72.49	72.52	72.68	72.55	72.55	73.17			
$\phi_{CC-C2}^d$	171.15	156.07	156.10	155.76	156.05	156.02	156.36			
$R_{vdw}(H1\cdots O)$	2.1734	2.1751	2.1825	2.1878	2.1846	2.1895	2.1908	2.229		
RC <i>a</i>	426.1025	396.3487	396.5789	399.2769	398.7133	399.0087	401.8968			
<i>b</i>	2.8025	2.7994	2.7922	2.8275	2.8253	2.8230	2.8265	2.785 163(28)	2.782 452	
<i>c</i>	2.7846	2.7829	2.7758	2.8108	2.8086	2.8062	2.8097	2.761 329(28)	2.762 228	

<sup>a</sup>Reference 8.<sup>b</sup>Reference 15.<sup>c</sup>Dihedral angle between the C2, C1, O and C1, O, H3 planes.<sup>d</sup>Angle between the C–C and  $C_2(H_2O)$  axes.

## B. Minima

### 1. Water acceptor structure (*Y*)

The optimal geometry and rotational constants (RC) of the water acceptor minimum (*Y*-structure) are listed in Table IV. The effect of monomer deformation due to complexation is quite small (cf. results in Tables II and IV), mainly manifested by a lengthening of 0.005 Å in the acetylene intramolecular C1–H1 distance (the H atom participating in the hydrogen bond). This change is almost universal among all levels of theory considered in this study.

The intermolecular A $\cdots$ W van der Waals equilibrium distance,  $R_{vdw}$ , was found to monotonically converge to  $R_e = 2.194$  Å at the MP2 level of theory with increasing basis set. The effect of higher electron correlation on this distance is small, of the order of 0.002 Å or less as evident from the comparison of the CCSD(T) values with the MP2 results for the aug-cc-pVTZ set (cf. Table IV). Therefore, our best estimate is  $R_e = 2.195$  Å. The experimentally available (vibrationally averaged) rotational constants and A $\cdots$ W van der Waals distance ( $R_0$ ) are also shown in Table IV. For a straightforward comparison of our best estimate of the computed equilibrium intermolecular separation ( $R_e = 2.195$  Å) with the one obtained from fitting the rotational constants to the experimentally measured microwave spectra ( $R_0 = 2.229$  Å), the effect of vibrational averaging should be included. This requires knowledge of a larger portion of the PES of the complex, a task beyond the goal of this study. However, our estimate of  $\Delta R = R_0 - R_e = 0.035$  Å for the magnitude of this effect is consistent with previous results for similar systems such as the water dimer.<sup>21</sup>

The value of the  $\phi_{C2C1O}$  angle indicates that the two carbon and the oxygen atoms do lie practically on a straight line (within  $<0.5^\circ$ ), therefore justifying the assumption made in obtaining the rotational constants (and subsequently the intermolecular separation  $R_0$ ) from experiment. The angle between the C–C and the  $C_2$  water axes,  $\phi_{cc,c2}$ , is  $156.0^\circ$ ,

almost insensitive to the level of correlation with basis sets of triple zeta or better quality. However, as noted in earlier studies,<sup>8,15</sup> it is anticipated that isomerization can occur following a path corresponding to a “rocking” motion of the water molecule via a structure (*YY*) having  $\phi_{cc,c2} = 180^\circ$  and higher ( $C_{2v}$ ) symmetry. Although the minimum on the PES has  $\phi_{cc,c2} < 180^\circ$ , the PES along the isomerization pathway varying this angle is extremely flat and inclusion of zero-point energies is required (*vide infra*) in order to obtain a more realistic picture of the minimum energy structure that is measured experimentally.

The harmonic vibrational frequencies of the AW complex are shown in Table V. Comparison of these with the ones for the isolated A and W species (cf. Table III) shows small shifts. At the MP2/aug-cc-pVTZ level, the water intramolecular bend is blue-shifted by  $\Delta\omega = 2$   $\text{cm}^{-1}$  in agreement with the measured<sup>14</sup>  $\Delta\nu = 4$   $\text{cm}^{-1}$  by Engdahl and Nelander. For the symmetric and antisymmetric OH stretches we calculate red-shifts of 3 and 5  $\text{cm}^{-1}$ , respectively. Miller and co-workers<sup>8</sup> have previously reported a measured red-shift of 1.15  $\text{cm}^{-1}$  for the water symmetric stretch and calculated a range of red-shifts from 5 to 12  $\text{cm}^{-1}$  with various basis sets of double zeta quality.

The shifts due to complexation are somewhat larger for the acetylene frequencies. The two doubly degenerate modes of A ( $\omega_4 = 601$   $\text{cm}^{-1}$  and  $\omega_5 = 754$   $\text{cm}^{-1}$  in Table III) corresponding to symmetric and antisymmetric bending, split in the AW complex to bands centered at 629, 634, 812, and 831  $\text{cm}^{-1}$  due to the broken cylindrical symmetry. The calculated blue-shifts of 28/33  $\text{cm}^{-1}$  for the acetylene  $\omega_4$  in the complex compare well with the measured<sup>14</sup> value of 20  $\text{cm}^{-1}$  for one of them. The corresponding blue shifts of 58/77  $\text{cm}^{-1}$  for  $\omega_5$  are also in accordance with the measured<sup>14</sup> ones of 49 and 56  $\text{cm}^{-1}$ .

TABLE V. Harmonic vibrational frequencies  $\omega$  ( $\text{cm}^{-1}$ ), IR Intensities ( $\text{km/mol}$ ), zero-point energies (ZPE,  $\text{kcal/mol}$ ) of the  $Y$ - and  $T$ -minima at the MP2/aug-cc-pVnZ,  $n=2, 3$  levels. Experimentally observed frequencies ( $\nu$ ) for the  $Y$ -minimum are also shown.

$Y$ -minimum					$T$ -minimum					
aug-cc-pVDZ			aug-cc-pVTZ		Exp <sup>a</sup>	aug-cc-pVDZ		aug-cc-pVTZ		
$\omega$	IR intensities	$\omega$	IR intensities	$\nu$		$\omega$	IR intensities	$\omega$	IR intensities	
$\omega_1(a')$	22	230	62	195	$\omega_1(a'')$	42	26	51	26	
$\omega_2(a'')$	74	30	67	21	$\omega_2(a')$	110	0.06	117	0.05	
$\omega_3(a')$	115	1.4	112	33	$\omega_3(a'')$	118	84	120	83	
$\omega_4(a')$	128	1.5	122	1.2	$\omega_4(a')$	183	77	197	77	
$\omega_5(a'')$	171	33	189	26	$\omega_5(a'')$	363	32	395	42	
$\omega_6(a')$	464	6.4	629	9.1	632	$\omega_6(a'')$	407	0.04	604	0.01
$\omega_7(a'')$	475	4.7	634	10	$\omega_7(a'')$	461	13	614	1.5	
$\omega_8(a')$	776	81	812	75	786	$\omega_8(a')$	705	91	755	86
$\omega_9(a'')$	790	87	831	76	793	$\omega_9(a')$	718	102	765	98
$\omega_{10}(a')$	1625	63	1630	69	1593.1	$\omega_{10}(a')$	1629	46	1633	48
$\omega_{11}(a')$	1938	8.4	1958	8.1	1969.6	$\omega_{11}(a')$	1942	0.3	1963	0.4
$\omega_{12}(a')$	3390	263	3392	257	3240.2	$\omega_{12}(a'')$	3424	109	3424	112
$\omega_{13}(a')$	3498	1.1	3509	3.3	3640.0	$\omega_{13}(a')$	3512	0.2	3523	0.2
$\omega_{14}(a')$	3802	9.1	3819	11	$\omega_{14}(a')$	3770	102	3782	126	
$\omega_{15}(a'')$	3935	80	3943	88	$\omega_{15}(a')$	3912	142	3920	149	
ZPE	30.31		31.03		ZPE	30.44		31.26		

<sup>a</sup>Reference 14.

For the  $\text{C}\equiv\text{C}$  stretching mode we calculate a red-shift of  $10\text{ cm}^{-1}$ , consistent with the observed<sup>14</sup> red-shift of  $4\text{ cm}^{-1}$  by Engdahl and Nelander. Finally we calculate red shifts of  $40$  and  $25\text{ cm}^{-1}$  for the C–H symmetric and antisymmetric stretching modes, respectively. The antisymmetric C–H stretch of the AW complex has been previously measured at  $3240\text{ cm}^{-1}$  in Ar matrices<sup>14</sup> and at  $3255\text{ cm}^{-1}$  in a nozzle expansion of a mixture of A in He and water.<sup>8</sup> The corresponding experimental red-shifts of the C–H antisymmetric acetylene stretch upon complexation in those two environments are  $63$  and  $34\text{ cm}^{-1}$ , respectively. Our estimate of  $\Delta\omega = 25\text{ cm}^{-1}$  is more in line with the result of the most recent experiment.<sup>8</sup> Our findings reinforce the argument originally proposed by Engdahl and Nelander<sup>14</sup> regarding the formation of a van der Waals type bond in which the water is acting as the proton acceptor based on the strongly red-shifted CH-stretching fundamental, the blue-shifted CH-deformation fundamental and the small shifts in the water frequencies upon complexation.

The minimum energies ( $E_e$ ), zero-point energies (ZPE) and energy differences ( $\Delta E_e$ ) also corrected for basis set superposition error (BSSE) are listed in Table VI. The lowest absolute energy,  $-153.582887$  hartree, is obtained at the MP4/aug-cc-pVQZ//MP4/aug-cc-pVTZ level (single point calculation). No optimizations were performed with the largest (aug-cc-pVQZ) set at either the MP4 or CCSD(T) levels since, due to the lack of analytical first derivatives for these methods, large CPU times are required for numerical optimizations. Nevertheless, the results of Table IV suggest that rather insignificant geometry changes are expected from such a calculation (cf. the difference between the MP2 and MP4 results of Table IV with the aug-cc-pVDZ and aug-cc-pVTZ basis sets).

As is evident from Table VI and Fig. 2, the energy difference,  $\Delta E_e$ , is practically method independent [MP2,

MP4, CCSD(T)], but varies with basis set from  $-3.6\text{ kcal/mol}$  (aug-cc-pVDZ) to  $-3.0\text{ kcal/mol}$  (aug-cc-pVQZ). Extrapolation to the CBS limit [Eq. (4)] for  $\Delta E_e$  (BSSE-corrected) produces values of  $-2.86$  and  $-2.87\text{ kcal/mol}$  at the MP2 and MP4 levels, respectively (Fig. 2). The extrapolated CBS values are, as expected, within  $<0.1\text{ kcal/mol}$  from the ones computed with the largest (aug-cc-pVQZ) set. Inclusion of zero-point energies amounts to corrections in the energy differences of  $1.03$  and  $0.95\text{ kcal/mol}$  at the MP2 level of theory with the aug-cc-pVDZ and aug-cc-pVTZ sets, respectively (cf. Tables III and VI). Our best estimate for the interaction energy of the  $Y$ -minimum is therefore  $-1.92\text{ kcal/mol}$ , obtained by adding the MP2/aug-cc-pVTZ  $\Delta(\text{ZPE})$  to the MP4 (BSSE-corrected) CBS limit. Finally the dipole moment of the  $Y$ -minimum at the MP2/aug-cc-pVTZ level is  $\mu = 2.376\text{ D}$ , in fair agreement with the experimentally obtained<sup>15</sup> value of  $2.0124(3)\text{ D}$  which, however, corresponds to the vibrationally averaged structure of higher symmetry (*vide infra*).

In lieu of the fact that our goal is to investigate larger clusters with more than one water molecule around acetylene, we found it compelling to assess the effect that the diffuse functions in the basis set have to the relative energetics. This was achieved by comparing the MP2 energy differences with the aug-cc-pVnZ and cc-pVnZ sets (augmented and plain, respectively).  $\Delta E_e$ 's obtained without diffuse functions are generally larger (on the negative scale) and have a larger BSSE correction than the ones obtained with the corresponding augmented sets. For example,  $\Delta E_e(\text{cc-pVDZ}) = -5.27\text{ kcal/mol}$  and  $\Delta E_e(\text{cc-pVTZ}) = -3.90\text{ kcal/mol}$  whereas the analogous values with the augmented sets are  $-3.61$  and  $-3.17\text{ kcal/mol}$ , respectively (cf. Table VI). Also since the plain sets have a larger BSSE correction than the augmented ones, this eventually results in almost the same BSSE-corrected  $\Delta E_e$  for the two sets. As

TABLE VI. Minimum energies ( $E_e$ , hartree), energy differences ( $\Delta E_e$ , kcal/mol) including corrections for basis set superposition error  $\Delta E_e$  (BSSE) and zero-point energies (ZPE), kcal/mol for the  $Y$ -,  $T$ -configurations and  $YY$ -,  $YT$ -, and  $TT$ -transition structures (t.s.). Subscript “0” denotes ZPE-corrected values.

Method	$E_e$	$\Delta E_e$	$\Delta E_e$ (BSSE)	ZPE	$\Delta E_0$	$\Delta E_0$ (BSSE)
<b>Y-structure</b>						
MP2	-153.359 654	-3.61	aug-cc-pVDZ -2.62	30.31	-2.58	-1.59
MP4	-153.401 763	-3.68	-2.62			-1.59 <sup>a</sup>
CCSD(T)	-153.401 078	-3.63	-2.61			-1.58 <sup>a</sup>
			aug-cc-pVTZ			
MP2	-153.498 094	-3.17	-2.72	31.03	-2.21	-1.77
MP4	-153.542 668	-3.22	-2.77			-1.82 <sup>a</sup>
CCSD(T)	-153.539 623	-3.20	-2.76			-1.81 <sup>a</sup>
			aug-cc-pVQZ			
MP2	-153.542 395	-2.97	-2.80			-1.85
MP4	-153.582 867	-2.98	-2.83			-1.88 <sup>b</sup>
<b>T-structure</b>						
			aug-cc-pVDZ			
MP2	-153.358 758	-3.04	-2.16	30.44	-1.88	-1.00
MP4	-153.400 814	-3.08	-2.12			-0.96 <sup>a</sup>
CCSD(T)	-153.400 034	-2.98	-2.05			-0.89 <sup>a</sup>
			aug-cc-pVTZ			
MP2	-153.497 859	-3.02	-2.56	31.26	-1.84	-1.38
MP4	-153.542 236	-2.95	-2.52			-1.34 <sup>a</sup>
CCSD(T)	-153.539 093	-2.87	-2.45			-1.27 <sup>a</sup>
			aug-cc-pVQZ			
MP2	-153.542 201	-2.85	-2.65			-1.47
MP4	-153.582 460	-2.73	-2.58			-1.40 <sup>b</sup>
<b>YY-t.s.</b>						
			aug-cc-pVDZ			
MP2	-153.359 654	-3.61	-2.61	30.28	-2.61	-1.61
MP4	-153.401 750	-3.67	-2.61			-1.61 <sup>a</sup>
CCSD(T)	-153.401 070	-3.63	-2.60			-1.60 <sup>a</sup>
			aug-cc-pVTZ			
MP2	-153.498 088	-3.16	-2.73	30.92	-2.33	-1.89
MP4	-153.542 645	-3.20	-2.77			-1.93 <sup>a</sup>
CCSD(T)	-153.539 606	-3.19	-2.77			-1.92 <sup>a</sup>
<b>TT-t.s.</b>						
			aug-cc-pVDZ			
MP2	-153.357 490	-2.25	-1.62	30.11	-1.42	-0.79
			aug-cc-pVTZ			
MP2	-153.496 392	-2.10	-1.84	30.88	-1.30	-1.04
<b>YT-t.s.</b>						
			aug-cc-pVDZ			
MP2	-153.358 526	-2.90	-2.05	30.32	-1.86	-1.01
			aug-cc-pVTZ			
MP2	-153.497 475	-2.78	-2.38	31.04	-1.81	-1.42

<sup>a</sup>Using MP2 ZPE's.

<sup>b</sup>Using the MP2/aug-cc-pVTZ ZPE's.

expected, the difference between the two families of sets (plain and augmented) decreases as the basis set increases since both eventually should converge to the same (CBS) limit.

## 2. Water donor structure (T)

The second minimum on the AW PES corresponds to a configuration in which the water molecule acts as the proton donor to the acetylene triple bond ( $T$ -structure of  $C_s$  symmetry in Fig. 1). Its optimal internal coordinates and rotational constants (RC) are listed in Table VII. As for the case of the  $Y$ -minimum, we find minimal changes in the fragment geometries upon complexation. The largest change is the lengthening of the water O–H bond that is pointing towards the triple bond by 0.003–0.004 Å. The van der Waals intermolecular distance (defined as the distance between the hydrogen bonded H atom of W and the center of the A triple bond) is 2.385, 2.345, and 2.346 Å at MP2/aug-cc-pVnZ,  $n = 2-4$  levels, respectively, and 2.397 (2.365) Å, 2.414

(2.378) Å at MP4 and CCSD(T)/ $n=2(3)$  levels, respectively (Table VII). It is interesting to note that electron correlation and quality of basis set have opposite effects on the magnitude of this distance: its magnitude decreases with basis set size while within a given basis set it increases with a better description of electron correlation [i.e., going from MP2 to MP4 and/or CCSD(T)]. Nevertheless it is practically converged with basis set at the triple zeta quality level (cf. the difference between the aug-cc-pVTZ and aug-cc-pVQZ results at the MP2 level). This distance was found to be larger than the corresponding intermolecular distance for the  $Y$ -minimum by about 0.18 Å. The hydrogen bond is almost linear with respect to the middle of the acetylene triple bond, deviating from 180° by 2.5° and 1.4° at the MP2/aug-cc-pVQZ and MP4/aug-cc-pVTZ levels, respectively. The results at the CCSD(T) level of theory are similar.

The harmonic vibrational frequencies and corresponding IR intensities at the MP2/aug-cc-pVnZ,  $n=2,3$  levels of theory, are shown in Table V. For the *in situ* water molecule,

TABLE VII. Optimal internal coordinates ( $\text{\AA}$ , degrees) and rotational constants (RC, in GHz) for the  $T$ -minimum.

	aug-cc-pVDZ			aug-cc-pVTZ			aug-cc-pVQZ
	MP2	MP4	CCSD(T)	MP2	MP4	CCSD(T)	MP2
$R_{C-C}$	1.2323	1.2336	1.2308	1.2131	1.2149	1.2110	1.2101
$R_{C-H}$	1.0759	1.0790	1.0794	1.0627	1.0649	1.0650	1.0622
$\phi_{H_2C_2C_1}$	179.64	179.77	179.79	179.72	179.89	179.90	179.71
$R_{H_3-O}$	0.9688	0.9696	0.9688	0.9648	0.9657	0.9643	0.9625
$R_{O-H_4}$	0.9657	0.9669	0.9664	0.9612	0.9627	0.9615	0.9587
$\phi_{H_3OH_4}$	103.82	103.79	103.84	104.13	104.05	104.16	104.29
$R_{H_3}^a$	2.3849	2.3969	2.4142	2.3446	2.3645	2.3782	2.3464
$\phi_{OH_3}^b$	178.51	180.00	180.00	177.52	178.63	179.32	177.54
$\phi_{H_3C_1H_1}$	104.68	104.66	104.51	104.61	104.52	104.38	104.57
RC $a$	32.1871	32.0538	32.1545	33.1426	33.0004	33.1462	33.2793
$b$	4.2583	4.2258	4.1848	4.3719	4.3162	4.2853	4.3727
$c$	3.8071	3.7797	3.7484	3.9103	3.8644	3.8417	3.9126

<sup>a</sup>Distance between the H3 of H<sub>2</sub>O and the middle of the triple bond (van der Waals distance).

<sup>b</sup>Angle between O–H3 and the middle of the triple bond.

the symmetric and antisymmetric stretching frequencies are red-shifted by 40 and 23  $\text{cm}^{-1}$  with respect to the isolated molecule as a result of its participation in the hydrogen bond and the subsequent elongation of one of the OH stretches by 0.003–0.004  $\text{\AA}$  as noted earlier. These shifts are an order of magnitude larger than the ones obtained for the  $Y$ -minimum.

The minimum energies, zero-point energies and energy differences also corrected for BSSE are listed in Table VI. The best calculated values are  $\Delta E_e = -2.73$  kcal/mol,  $\Delta E_e(\text{BSSE-corrected}) = -2.58$  kcal/mol and  $\Delta E_0(\text{BSSE-corrected}) = -1.40$  kcal/mol at the MP4/aug-cc-pVQZ//MP4/aug-cc-pVTZ level of theory. The variation of the energy difference with basis set is illustrated in Fig. 3. Extrapolation of the BSSE-corrected energy differences yields  $\Delta E_{e/\text{CBS}}(\text{BSSE-corrected}) = -2.59$  kcal/mol, whereas accounting for zero-point energy differences [ $\Delta(\text{ZPE}) = 1.18$  kcal/mol at the MP2/aug-cc-pVTZ level] yields  $\Delta E_{0/\text{CBS}}(\text{BSSE-corrected}) = -1.41$  kcal/mol. Finally we obtained a dipole moment of 2.115 D at the MP2/aug-cc-pVTZ level of theory for the  $T$ -minimum.

The water donor ( $T$ ) minimum is, therefore, less stable than the water acceptor ( $Y$ ) minimum by  $\sim 0.5$  kcal/mol. This result is consistent with the realization that a comparison between the experimentally measured RC and the ones com-

puted for the  $Y$ - and  $T$ -minima (cf. Tables IV and VII) suggests that the observed structure definitively corresponds to the water acceptor  $Y$ -rather than the water donor  $T$ -structure. Furthermore, the stability of the  $T$  minimum also depends upon the height of the barrier corresponding to the isomerization between the two, an issue addressed later in this study.

## C. Transition states

In this section we will investigate the isomerization of the  $Y$ -minimum via a highly symmetric ( $C_{2v}$ ) configuration ( $YY$ ), the isomerization of the  $T$ -minimum corresponding to the exchange of the water H atoms that are hydrogen bonded to the triple bond of acetylene ( $TT$ ) and the transition state between the two minima ( $YT$ ).

### 1. $YY$ -structure ( $C_{2v}$ )

As noted earlier, isomerization between the two  $C_s$  mirror images of the  $Y$ -minimum can occur via a ‘‘rocking’’ motion of the water molecule. The transition state (t.s.) for this process has, therefore,  $C_{2v}$  symmetry. Its optimal internal coordinates are shown in Table VIII and the harmonic vibrational frequencies and IR intensities in Table IX. Ex-

TABLE VIII. Optimal geometry ( $\text{\AA}$ , degrees) and rotational constants RC (GHz) of the  $YY$ -configuration ( $C_{2v}$  symmetry).

	aug-cc-pVDZ			aug-cc-pVTZ		
	MP2	MP4	CCSD(T)	MP2	MP4	CCSD(T)
$R_{C-C}$	1.2325	1.2332	1.2311	1.2132	1.2153	1.2114
$R_{C_1-H_1}$	1.0800	1.0828	1.0831	1.0658	1.0686	1.0685
$R_{H_2-C_2}$	1.0747	1.0778	1.0782	1.0607	1.0643	1.0643
$R_{H-O}$	0.9657	0.9667	0.9662	0.9612	0.9627	0.9617
$\phi_{H_3OH_4}$	104.29	104.33	104.37	104.22	104.53	104.64
$R_{C_1\cdots O}$	3.2527	3.2528	3.2603	3.2528	3.2486	3.2532
$R_{\text{vdw } H_1\cdots O}$	2.1726	2.1700	2.1772	2.1871	2.1801	2.1848
RC $a$	431.2743	430.0592	430.2625	433.5681	432.4438	432.7931
$b$	2.8026	2.7994	2.7923	2.8277	2.8244	2.8222
$c$	2.7845	2.7813	2.7743	2.8093	2.8060	2.8039



TABLE IX. Harmonic vibrational frequencies  $\omega$  ( $\text{cm}^{-1}$ ), IR intensities ( $\text{km}/\text{mol}$ ) and zero-point energies (ZPE,  $\text{kcal}/\text{mol}$ ) of the  $YY$ -t.s. at the MP2/aug-cc-pVnZ,  $n=2, 3$  level.

	aug-cc-pVDZ		aug-cc-pVTZ	
	$\omega$	IR intensities	$\omega$	IR intensities
$\omega_1(b_1)$	16i	232	38i	229
$\omega_2(b_2)$	74	32	63	31
$\omega_3(b_1)$	114	0.7	102	0.5
$\omega_4(a_1)$	129	1.5	122	1.4
$\omega_5(b_2)$	170	34	183	32.6
$\omega_6(b_1)$	464	6.6	628	9.3
$\omega_7(b_2)$	475	4.7	633	10.0
$\omega_8(b_1)$	777	81	809	73
$\omega_9(b_2)$	791	87	828	77
$\omega_{10}(a_1)$	1625	63	1630	67
$\omega_{11}(a_1)$	1938	8.4	1959	8.1
$\omega_{12}(a_1)$	3391	262	3395	254
$\omega_{13}(a_1)$	3498	1.1	3510	4.1
$\omega_{14}(a_1)$	3803	9.0	3820	11
$\omega_{15}(b_2)$	3935	80	3945	89
ZPE		30.28		30.92

amination of the harmonic vibrational frequencies readily confirms that the structure is a first-order transition state having one imaginary frequency ( $b_1$  symmetry) equal to  $16i$  and  $38i \text{ cm}^{-1}$  at the MP2 level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. The rest of the 14 harmonic frequencies are practically identical (within  $1\text{--}3 \text{ cm}^{-1}$  for the ones larger than  $800 \text{ cm}^{-1}$ ) with those of the  $Y$ -minimum (Table V). The inversion barrier is  $<0.02 \text{ kcal}/\text{mol}$  ( $\sim 5 \text{ cm}^{-1}$ ) at the MP4/aug-cc-pVTZ level of theory, a value consistent with the one previously reported by Miller and co-workers<sup>8</sup> ( $5.9 \text{ cm}^{-1}$ ).

The geometries of the  $YY$  and  $Y$  stationary points are essentially identical at all levels of calculation. The results of Table IV and VIII suggest that the most significant geometry change is the shortening of the  $\text{HCCH}\cdots\text{OH}_2$  van der Waals distance by  $0.004 \text{ \AA}$  in the  $YY$ -t.s. when compared to the  $Y$ -minimum (MP4/aug-cc-pVTZ level).

Notwithstanding the fact that the  $YY$  stationary point is a transition state on the BSSE-uncorrected energy surface (with a barrier of  $\sim 5 \text{ cm}^{-1}$  with respect to  $Y$ ), correcting for BSSE was found to reverse the order, stabilizing the  $YY$  more than the  $Y$  geometry albeit by a negligible amount ( $0.4 \text{ cm}^{-1}$  at the MP4/aug-cc-pVTZ level of theory, cf. Table VI). This suggests that BSSE corrections qualitatively alter the subtle features of the PES in the vicinity of the minimum, a fact that has been overlooked during earlier studies. Based on our results we suggest that the previously assumed double well potential used to describe the high amplitude motion of the water molecule off the acetylene  $C_2$  axis, should in fact be replaced with a single well potential with the minimum at the  $C_{2v}$  geometry. This potential is quite flat and inclusion of zero-point energy corrections tends to continue the trend of stabilizing the  $YY$ -with respect to the  $Y$ -stationary point. As can be seen from Table VI, the  $\Delta E_0(YY-Y)$  is  $0.12 \text{ kcal}/\text{mol}$  ( $YY$  more stable). This energy difference is almost identical (within  $0.01 \text{ kcal}/\text{mol}$ ) at the MP2, MP4, and CCSD(T)

levels of theory with the aug-cc-pVTZ set (Table VI). In order to obtain an accurate value for the interaction energy we note (Table VI) that the variation of  $\Delta E_e$  for the  $Y$ - and  $YY$ -structures with respect to the isolated fragments is almost identical both as a function of basis set and electron correlation. By using the extrapolated CBS value for  $\Delta E_e$  of the  $Y$ -minimum ( $-2.87 \text{ kcal}/\text{mol}$ , previously obtained in Sec. III B 1) and adding a  $\Delta(\text{ZPE})=0.83 \text{ kcal}/\text{mol}$  (MP2/aug-cc-pVTZ) we arrive at a value of  $-2.04 \text{ kcal}/\text{mol}$  (including BSSE corrections) for the interaction energy of the  $YY$ -structure. This value is lower than the one previously obtained using the same procedure for the  $Y$ -minimum ( $-1.92 \text{ kcal}/\text{mol}$ ), mainly due to differences in the zero-point energies as noted earlier. It is, therefore, justified to suggest that the ‘‘structure’’ of the water acceptor arrangement, although extremely floppy with respect to the rocking of the  $W$  molecule off the acetylene  $C_2$  axis, has a structure of  $C_{2v}$  symmetry. The dipole moment of the  $YY$ -stationary point is  $2.418 \text{ D}$  (MP2/aug-cc-pVTZ), slightly larger than the one for the  $Y$ -structure.

## 2. $TT$ -structure

This transition state arises from the isomerization of the  $T$ -minimum by allowing the ‘‘hydrogen bonded’’ H atom of  $W$  to become ‘‘free’’ and vice versa. It has  $C_{2v}$  symmetry with the two acetylene hydrogen atoms pointing slightly upwards,  $\varphi(\text{HCC})=179.82^\circ$ , at the MP2/aug-cc-pVTZ level [Fig. 1(d)]. Its internal coordinates are shown in Table X at the MP2/aug-cc-pVnZ,  $n=2,3$  levels. The only geometric change worth mentioning is the decrease of the water HOH angle by  $1.6^\circ$  with respect to the geometry of the  $T$ -minimum. Its harmonic frequencies are listed in Table XI. The imaginary frequency ( $174i \text{ cm}^{-1}$ ) corresponds to an oscillating motion of the water plane transversely to the  $C\text{--}C$  axis. A comparison between the harmonic frequencies of the  $T$ -minimum and the  $TT$ -t.s. (Tables V and XI) reveals that most of the change ( $29\text{--}93 \text{ cm}^{-1}$ ) occurs in the low intermolecular modes. The intramolecular modes remain almost unperturbed except the water symmetric stretch ( $\omega_{14}$ ) for which we observe a red-shift of  $40 \text{ cm}^{-1}$  with respect to the  $T$ -minimum. This is consistent with the formation of a ‘‘double donor’’ arrangement of the water to the acetylene triple bond.

The energetics of the  $TT$ -t.s. are shown in Table VI. The best computed number (including ZPE corrections) for the barrier corresponding to the isomerization of the  $T$ -minimum via the  $TT$ -t.s. is  $0.34 \text{ kcal}/\text{mol}$  ( $0.54 \text{ kcal}/\text{mol}$  for BSSE-uncorrected) at the MP2/aug-cc-pVTZ level.

## 3. $YT$ -structure

The transition state [Fig. 1(e)] between the  $Y$ - and  $T$ -minima has no symmetry elements ( $C_1$ ). Its internal coordinates, harmonic frequencies and energies are listed in Tables X, XI, and VI, respectively. The imaginary frequency of this first order t.s. is  $39i$  and  $78i$  at the MP2 level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. Although no significant shifts were found for the A frequen-

TABLE X. Geometry (Å, degrees) and rotational constants RC (GHz) of the *TT*- and *YT*-t.s..

	<i>TT</i> transition state		<i>YT</i> transition state		
	aug-cc-pVDZ MP2	aug-cc-pVTZ MP2	aug-cc-pVDZ MP2	aug-cc-pVTZ MP2	
$R_{C-C}$	1.2322	1.2129	$R_{C-C}$	1.2322	1.2130
$R_{C1-H1}$	1.0759	1.0626	$R_{C1-H1}$	1.0763	1.0631
$R_{H2-C2}$	1.0759	1.0626	$R_{H2-C2}$	1.0756	1.0624
$\phi_{H2C2C1}$	179.75	179.82	$\phi_{H2C2C1}$	178.46	179.21
$\phi_{C2C1H1}$	179.75	179.82	$\phi_{C2C1H1}$	178.43	179.49
$\delta_{H1C1C2H2}^a$	0.0	0.0	$\delta_{H1C1C2H2}^a$	174.25	180.00
$R_{H3-O}$	0.9665	0.9621	$R_{H3-O}$	0.9684	0.9645
$R_{H4-O}$	0.9665	0.9621	$R_{H4-O}$	0.9654	0.9611
$\phi_{H3OH4}$	102.32	102.49	$\phi_{H3OH4}$	104.33	104.56
$R_{H3}^b$	2.8828	2.8721	$R_{C1\cdots O}$	3.1860	3.1947
$\phi_{H3C1C2}$	77.94	78.08	$\phi_{C2C1O}$	99.77	96.33
$\delta_{H3C1C2H2}$	164.86	164.86	$\phi_{H3OC1}$	31.901	27.43
$\phi_{OH3}^{\equiv}$	113.70	113.61	$\delta_{OC1C2H1}^a$	0.36	0.00
$\delta_{OH3C1C2}$	95.24	95.16	$\delta_{H3OC1C2}^a$	175.36	180.00
$\delta_{H4OH3}^{\equiv}$	0.0	0.0	$\delta_{H4OH3C1}^a$	169.60	180.00
			$R_{H3-C1}$	2.4187	2.3805
			$R_{H3-C2}$	2.6680	2.5869
			$R_{H}^{\equiv}$	2.4707	2.4107
			$R_{H1\cdots O}$	3.1566	3.2396
RC <i>a</i>	31.5420	32.4442	RC <i>a</i>	36.9169	36.3345
<i>b</i>	4.2395	4.2752	<i>b</i>	4.1802	4.2903
<i>c</i>	3.8014	3.8427	<i>c</i>	3.7575	3.8372

<sup>a</sup>Dihedral angle between the two planes defined from the first and the last three designated atoms.<sup>b</sup>The symbol  $\equiv$  denotes the middle of the triple bond.

cies, the W stretches show red-shifts of  $38(\omega_{14})$  and  $23(\omega_{15})$   $\text{cm}^{-1}$  with respect to isolated water at the MP2/aug-cc-pVTZ level.

The energy barrier for the isomerization between the *Y*- and *T*-minima via the *YT*-t.s. (cf. Table VI) [with respect to the less stable *T*-minimum] is quite small, 0.24 kcal/mol (BSSE uncorrected) and 0.18 kcal/mol (BSSE-corrected) at the MP2/aug-cc-pVTZ level. Inclusion of ZPE corrections, however, drastically alters this picture resulting in no barrier between the two minima. Therefore, the

*T*-minimum is unstable since it readily collapses to the more stable *Y*-structure. This is because  $\Delta E_0[(Y) - (YT)/\text{BSSE-uncorrected}] = 0.03$  kcal/mol but  $\Delta E_0[(Y) - (YT)/\text{BSSE-corrected}] = -0.04$  kcal/mol at the MP2/aug-cc-pVTZ level. This result is consistent with the observation of only one minimum (*Y*-structure) experimentally.

#### IV. REMARKS AND CONCLUSIONS

We have performed extensive *ab initio* calculations on the acetylene–water dimer PES employing MP2, MP4, and

TABLE XI. Harmonic vibrational frequencies  $\omega$  ( $\text{cm}^{-1}$ ), IR intensities (km/mol) and zero-point energies (ZPE, kcal/mol) of the *TT*- and *YT*-t.s..

	<i>TT</i> transition state				<i>YT</i> transition state				
	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVDZ		aug-cc-pVTZ		
	$\omega$	IR intensities	$\omega$	IR intensities	$\omega$	IR intensities	$\omega$	IR intensities	
$\omega_1(b_1)$	151 <i>i</i>	89	174 <i>i</i>	89	$\omega_1$	39 <i>i</i>	117	78 <i>i</i>	123
$\omega_2(b_2)$	24	11	29	10.0	$\omega_2$	59	34	54	15
$\omega_3(a_1)$	95	0.08	91	0.1	$\omega_3$	104	3.3	108	1.2
$\omega_4(a_2)$	155	0.00	157	0.00	$\omega_4$	246	105	253	103
$\omega_5(b_2)$	293	135	302	143	$\omega_5$	315	44	313	49
$\omega_6(a_2)$	415	0.00	607	0.00	$\omega_6$	409	0.02	603	0.2
$\omega_7(b_2)$	431	7.4	607	0.89	$\omega_7$	454	1.6	615	0.4
$\omega_8(b_1)$	708	90	757	85	$\omega_8$	706	97	755	92
$\omega_9(a_1)$	710	102	759	98	$\omega_9$	719	99	765	96
$\omega_{10}(a_1)$	1626	139	1630	142	$\omega_{10}$	1627	39	1631	35
$\omega_{11}(a_1)$	1942	0.08	1964	0.10	$\omega_{11}$	1942	0.2	1964	0.3
$\omega_{12}(b_2)$	3424	105	3424	108	$\omega_{12}$	3424	107	3424	110
$\omega_{13}(a_1)$	3512	0.09	3524	0.08	$\omega_{13}$	3512	0.08	3522	0.1
$\omega_{14}(a_1)$	3803	11	3821	13	$\omega_{14}$	3774	62	3784	92
$\omega_{15}(b_1)$	3922	49	3931	50	$\omega_{15}$	3919	132	3924	146
ZPE		30.11		30.88	ZPE		30.32		31.04

CCSD(T) methods coupled with a series of increasing size basis sets, aug-cc-pVnZ,  $n=2,3,4$ . We have systematically examined five possible van der Waals isomers labeled *Y*, *YY*, *T*, *TT*, and *YT* (*vide supra*), with the main goals of (i) establishing accurate interaction energies and geometries (ii) understanding the multidimensional PES and the isomerization mechanisms between the various stationary points in order to explain the available experimental data. Our salient findings can be summarized as follows.

- (1) The global minimum on the PES corresponds to a configuration in which the water molecule acts as the proton acceptor from one of the acetylene hydrogen atoms, in agreement with previous studies. The PES with respect to the rocking of the water molecule off the acetylene  $C_2$  axis is quite flat and its features are sensitive to the theoretical treatment. On the BSSE-uncorrected PES the equilibrium geometry at all levels considered here [MP2, MP4, CCSD(T)] corresponds to a configuration of  $C_s$  symmetry (the angle between the C–C and the water  $C_2$  axes is  $156.0^\circ$ ) with a barrier of  $\sim 5 \text{ cm}^{-1}$  with respect to isomerization via the highly symmetric planar arrangement of  $C_{2v}$  symmetry. However, accounting for BSSE qualitatively alters this double-well picture producing a single minimum at the  $C_{2v}$  arrangement. In any event even the double well potential on the BSSE-uncorrected surface does not support a vibrational level and inclusion of zero-point energy corrections results in the  $C_{2v}$  configuration being more stable. The two structures, namely *Y* and *YY*, are for all practical purposes indistinguishable, and we can think of the AW complex as an extremely floppy, quasiplanar system with an interaction that is weaker than that of a typical hydrogen bond.<sup>27</sup> Our best estimate for the binding energy (corrected for BSSE and ZPE) is  $-2.04 \text{ kcal/mol}$  at a van der Waals distance  $R_{\text{vdWHI}\cdots\text{O}} = 2.190 \text{ \AA}$ .
- (2) The configuration in which the water molecule acts as a proton donor to the acetylene triple bond corresponds to a local minimum on the PES with a van der Waals distance from the middle of the  $\text{C}\equiv\text{C}$  bond of  $2.365 \text{ \AA}$  (MP4/aug-cc-pVTZ). The water molecule can interchange its hydrogen atoms by moving transversely to the acetylenic triple bond; the corresponding barrier for this process ( $T \rightarrow TT \rightarrow T$ ) is  $0.34 \text{ kcal/mol}$ . The barrier for isomerization to the global minimum was found to be just  $0.18 \text{ kcal/mol}$ . However, by including BSSE and ZPE corrections the energy of *YT* is lower than that of *T* ( $\Delta E_0 = -1.41 \text{ kcal/mol}$ ) by  $0.04 \text{ kcal/mol}$ . This means that it can easily slip to the global minimum, and this is the reason why only one minimum (*YY*) has been observed experimentally.
- (3) Although the *T*-structure does not correspond to a local minimum on the PES (destabilized by BSSE and mainly by ZPE corrections) it, nevertheless, represents an important binding site that can be accessed in clusters of acetylene with more than one water molecules via the formation of cyclic homodromic water networks, as it will be seen in a future study.<sup>28</sup> Establishing accurate relative energy differences between the two main bond-

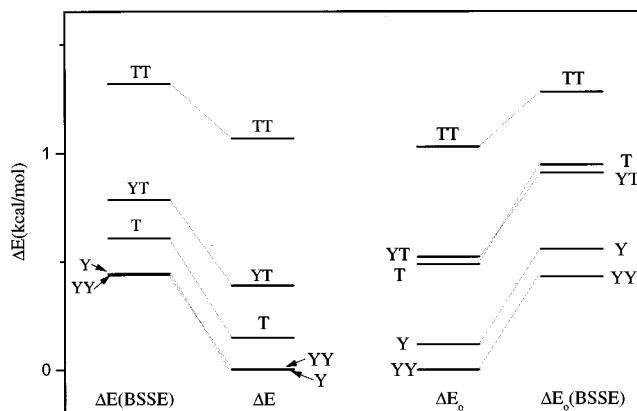


FIG. 4. Relative energy levels (MP2/aug-cc-pVTZ) of the various stationary points on the PES.

ing scenarios (*Y*- vs *T*-) considered here is quite important in the development and parametrization of accurate interaction potentials used to study the microsolvation of acetylene. A previous analysis<sup>13</sup> has indicated that the main term in the perturbation expansion for both structures is the electrostatic interaction with the next most important term being the exchange repulsion; this term was found to be more repulsive for the *Y*- than for the *T*-arrangement. Charge-transfer terms were reported to have different contributions for the two arrangements as water is an electron donor in the *Y*- and an electron acceptor in the *T*-structure, respectively. A simple hard-sphere electrostatic model,<sup>13,16</sup> previously used to probe the two isomers, reproduces the interaction energy for the *Y*-arrangement quite accurately ( $-3.09 \text{ kcal/mol}$ ) when compared to *ab initio* ( $-2.87 \text{ kcal/mol}$ ). However, it yields an energy separation of  $1.6 \text{ kcal/mol}$  between the two isomers a value that is larger than the one obtained here ( $0.3 \text{ kcal/mol}$ ).

- (4) An issue that has been overlooked in all previous studies is the effect of BSSE on the ground-state PES. We found that inclusion of BSSE corrections (i) alters the equilibrium geometry of the global minimum and the features of the PES around it and (ii) destabilizes the *T*-minimum with respect to the global minimum, a fact that is enhanced by the inclusion of ZPE corrections as discussed in point (2) above.
- (5) The effects of higher than MP2 level of correlation on the binding energy and structure are quite small. Accurate energetics can be obtained using a triple zeta quality basis set that includes diffuse functions. A comprehensive summary of the relative energetics of all five isomers at the MP2/aug-cc-pVTZ level of theory is shown in Fig. 4.

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