

# Exploring the interaction of the water dimer with a helium atom. Geometry and interaction properties of the $(\text{H}_2\text{O})_2\cdot\text{He}$ weakly bound molecule

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## Abstract

We report an investigation of the molecular geometry of the weakly bound  $(\text{H}_2\text{O})_2\cdot\text{He}$  complex. We have determined the most stable configuration of the system relying on second-order Møller-Plesset perturbation theory calculations with large, flexible basis sets. Our findings are in essential agreement with previous experimental work on the analogous  $(\text{H}_2\text{O})_2\cdot\text{Ar}$ . We have also obtained induced dipole moments for the complex from Møller-Plesset perturbation theory, coupled cluster and density functional theory calculations. At the highest CCSD(T) level of theory a [6s4p3d1f/4s3p1d/6s4p3d] basis set yields a total interaction dipole moment of  $\mu_{\text{int}} = 0.0096$  ea<sub>0</sub>.

Given the universal importance of the water molecule [1] the structure and properties of water clusters constitutes a profoundly interesting research field. Although most of the investigations focus on structure and energetics [2-6] the electric properties of  $(\text{H}_2\text{O})_n$  have also attracted particular attention [7-10]. The electric dipole moment, polarizability and hyperpolarizability of the monomer [11-14] and the dimer [15,16] have been studied more extensively. The electric properties of  $(\text{H}_2\text{O})_n$  are particularly relevant to a new class of studies where the cluster is considered as an autonomous unit in interaction with other systems [17-26].

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In this paper we turn our attention to the  $(\text{H}_2\text{O})_2\text{He}$  complex, the smallest possible  $(\text{H}_2\text{O})_2\text{Rg}_n$  type cluster. Previous experimental studies have been reported for the analogous  $(\text{H}_2\text{O})_2\text{Ar}$  [18, 23]. We note also an excellent recent theoretical study on  $(\text{H}_2\text{O})_2\text{Ar}_n$  [25]. Our aim in this project is the systematic exploration of the interaction of  $(\text{H}_2\text{O})_2$  with He. We thus judge both informative and instructive to explore large portions of the relevant potential energy surface. In addition we expect to locate the most stable configuration of the  $(\text{H}_2\text{O})_2\text{He}$  weakly bound complex and to determine the interaction dipole moment. Our approach to the calculation of interaction-induced properties has been presented in sufficient detail in previous work [27-29]. The interaction property of  $A\cdots B \equiv (\text{H}_2\text{O})_2\text{He}$  is calculated as

$$P_{\text{inter}} = P[(\text{H}_2\text{O})_2 \dots \text{He}] - P[(\text{H}_2\text{O})_2 \dots \text{X}] - P[\text{X} \dots \text{He}] \quad (1)$$

where  $P(A \dots X)$  etc denote calculations of the property for subsystem A in the presence of the ghost orbitals of subsystem B. In this approach the calculation of the total dipole moment requires particular attention. The components  $\mu$  of the interaction dipole moment are obtained separately as

$$\mu_\alpha = \mu_\alpha[(\text{H}_2\text{O})_2 \dots \text{He}] - \mu_\alpha[(\text{H}_2\text{O})_2 \dots \text{X}] - \mu_\alpha[\text{X} \dots \text{He}] \quad (2)$$

The total interaction dipole moment is subsequently defined as

$$\mu_{\text{int}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

The conventional ab initio methods employed in the present work are self-consistent field (SCF), second- and fourth-order Møller-Plesset Perturbation Theory (MP2 and MP4, respectively), singles and doubles coupled cluster (CCSD) and single and double excitation coupled cluster theory including an estimate of connected triple excitations via a perturbational treatment (CCSD(T)) [30,31]. We also use standard, widely used density functional methods as B3LYP, B3P86 and B3PW91 [32]. The gaussian-type basis sets (see Table 1) used in the calculations are taken from previous work [12,16,27]. Full details

Table 1: Basis sets used in the calculations on  $(\text{H}_2\text{O})_2\text{He}$ 

Basis set	Subsystem		GTF
	$\text{H}_2\text{O}$	He	
D0	[6s4p2d/4s2p]	[6s4p3d]	129
D1	[6s4p3d/4s2p]	[6s4p3d]	139
D2	[6s4p3d/4s3p1d]	[6s4p3d]	171
D3	[6s4p3d1f/4s3p1d]	[6s4p3d]	185
Q1	[9s6p6d3f/6s4p2d1f]	[6s4p3d]	329
Q2	[9s6p6d4f/6s5p3d2f]	[6s4p3d]	403
Q3	[9s6p6d4f/6s5p3d2f]	[6s4p3d1f]	410

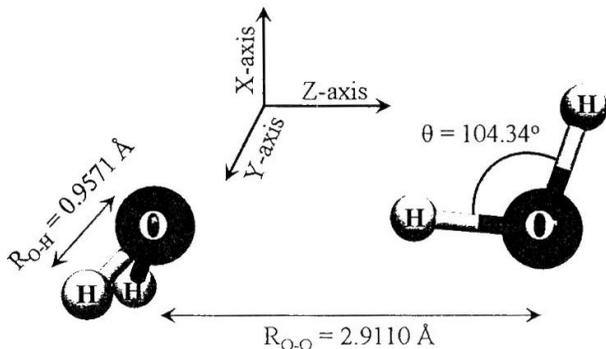


Figure 1: Adopted molecular geometry for the water dimer

of their composition will be given elsewhere [33]. The molecular geometry of the water dimer used in this work (see Figure 1) is the one used in our previous work [16]. Atomic units are used throughout this paper, unless otherwise specified [34]. The GAUSSIAN 94 [35] and GAUSSIAN 98 [36] programmes have been used in all calculations.

All basis sets for the  $(\text{H}_2\text{O})_2$  and He subsystems in Table 1 have been specifically designed for electric polarizability calculations. We expect them, as we may, to be able to account properly for the  $(\text{H}_2\text{O})_2\text{He}$  interaction. We have based our search for the global minimum of the potential energy surface on the MP2 method (all electrons correlated). The basis

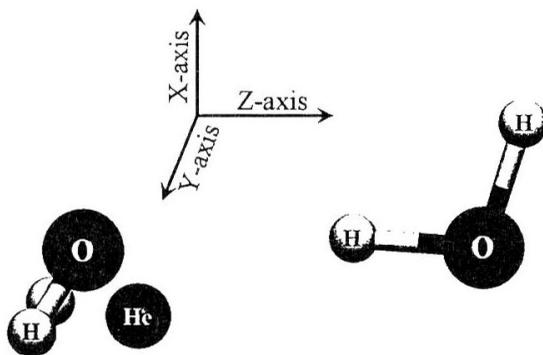


Figure 2: Most stable molecular geometry of the complex  $(\text{H}_2\text{O})_2 \text{He}$

Table 2: Geometrical parameters and interaction energies for the most stable configuration of the complex  $(\text{H}_2\text{O})_2 \text{He}$  calculated at the MP2(Full) level of theory

Basis Set	X / $\alpha_0$	Y / $\alpha_0$	Z / $\alpha_0$	$E_{\text{int}} / E_{\text{h}}$
D0	-0.267	6.064	1.234	-0.000137429
D1	-0.248	6.059	1.236	-0.000138335
D3	-0.010	5.985	1.299	-0.000148083

sets used in this search are D0  $\equiv$  [6s4p2d/4s2p/6s4p3d], D1  $\equiv$  [6s4p3d/4s2p/6s4p3d] and D3  $\equiv$  [6s4p3d1f/4s3p1d/6s4p3d]. The most stable geometry of the complex in each case is specified by the position of the He atom with reference to the  $(\text{H}_2\text{O})_2$  subsystem. Our values in Table 2 show that the addition of the diffuse d-GTF on the oxygen center for  $(\text{H}_2\text{O})_2$  has a rather small effect on the geometry of the complex and the total interaction energy  $E_{\text{int}}$ . The most affected part is the x coordinate (see Table 2) which shows a trend bringing the He atom closer to the yz plane. This trend is clearly confirmed for the MP2(Full)/D3 calculations. We clearly observe that the He atom lies now very close to the yz plane although the projection of the position onto the plane has not changed dramatically: the x coordinate changes from -0.248 to -0.010  $a_0$  while the change for y and z is -0.074 and 0.063  $a_0$ , respectively. Our best value for  $E_{\text{int}}$  is -0.000148083  $E_h$ .

We have collected in Table 3 the calculated values for the dipole moment of the complex, the water dimer and the interaction properties  $\mu$  and  $\mu_{\text{nt}}$ . All values for the complex pertain to the MP2(Full)/D3 geometry. The water dimer geometry is the one previously used [16]. We expect our large Q3 basis set to yield reference SCF and MP2 values for the all calculated properties. The MP2/Q3 results for  $\mu_{\text{nt}}$  are 0.0092 and 0.0097  $e a_0$ , respectively. All other basis sets are in very close agreement with these values. The highest level of theory used in the dipole moment calculations is CCSD(T). Thus our best values for  $\mu$  and  $\mu_{\text{nt}}$  are the CCSD(T)/D3 ones  $\mu = 0.0027$ ,  $\mu = 0.0056$ ,  $\mu = 0.0073$  and  $\mu_{\text{nt}} = 0.0096$   $e a_0$ . It is worth noticing that the values obtained with all other correlated methods MP2, MP4 and CCSD do not differ significantly from the above. Last, it is clear that all DFT method systematically overestimate the interaction dipole moment. The difference is rather small in absolute terms.

In conclusion, we have shown that the most stable geometry for the  $(\text{H}_2\text{O})_2\text{He}$  complex bears a strong resemblance to that obtained by Arunan et al [18] for the analogous  $(\text{H}_2\text{O})_2\text{Ar}$ . In both cases the rare gas atom is located at the side of the water dimer. The

Table 3. Total dipole moment of the  $(\text{H}_2\text{O})_2 \dots \text{He}$  complex, the water dimer  $(\text{H}_2\text{O})_2 \dots \text{He}$  and the interaction dipole moment of the complex  $(\text{H}_2\text{O})_2 \dots \text{He}$ . All values for the complex pertain to the MP2(Full)/D3 geometry (see Table 2). Reference ab initio results are given in bold characters.

Basis set	Method	$\mu((\text{H}_2\text{O})_2 \dots \text{He})$	$\mu((\text{H}_2\text{O})_2)$	Interaction dipole moment				
				$\mu_x$	$\mu_y$	$\mu_z$	$\mu_{int}$	
D0	SCF	1.0719	1.0788	0.0027	0.0054	0.0070	0.0093	
	MP2	1.0227	1.0292	0.0027	0.0060	0.0073	0.0098	
	MP4	1.0099	1.0164	0.0027	0.0059	0.0073	0.0098	
	CCSD	1.0197	1.0263	0.0027	0.0057	0.0073	0.0097	
	CCSD(T)	1.0136	1.0202	0.0027	0.0058	0.0073	0.0097	
	B3LYP	1.0439	1.0514	0.0030	0.0061	0.0078	0.0104	
	B3P86	1.0453	1.0526	0.0030	0.0064	0.0077	0.0105	
	B3PW91	1.0436	1.0509	0.0029	0.0069	0.0077	0.0107	
	D1	SCF	1.0727	1.0799	0.0027	0.0054	0.0070	0.0093
		MP2	1.0244	1.0318	0.0027	0.0060	0.0073	0.0098
MP4		1.0115	1.0188	0.0027	0.0059	0.0073	0.0097	
CCSD		1.0211	1.0284	0.0027	0.0057	0.0073	0.0097	
CCSD(T)		1.0151	1.0224	0.0027	0.0057	0.0073	0.0097	
B3LYP		1.0444	1.0524	0.0030	0.0061	0.0078	0.0104	
B3P86		1.0459	1.0538	0.0030	0.0064	0.0077	0.0105	
B3PW91		1.0443	1.0521	0.0029	0.0069	0.0077	0.0107	
D2		SCF	1.0714	1.0785	0.0027	0.0054	0.0070	0.0092
		MP2	1.0230	1.0304	0.0027	0.0060	0.0073	0.0098
	MP4	1.0106	1.0180	0.0027	0.0058	0.0073	0.0097	
	CCSD	1.0206	1.0280	0.0027	0.0056	0.0073	0.0096	
	CCSD(T)	1.0145	1.0219	0.0027	0.0057	0.0073	0.0096	
	B3LYP	1.0433	1.0513	0.0030	0.0060	0.0079	0.0104	
	B3P86	1.0444	1.0524	0.0030	0.0064	0.0078	0.0105	
	B3PW91	1.0427	1.0506	0.0029	0.0069	0.0077	0.0107	
	D3	SCF	1.0695	1.0765	0.0027	0.0054	0.0070	0.0092
		MP2	1.0214	1.0287	0.0027	0.0059	0.0073	0.0098
MP4		1.0093	1.0166	0.0028	0.0057	0.0073	0.0097	
CCSD		1.0190	1.0263	0.0027	0.0056	0.0073	0.0096	
CCSD(T)		1.0130	1.0204	0.0027	0.0056	0.0073	0.0096	
B3LYP		1.0427	1.0507	0.0030	0.0060	0.0079	0.0104	
B3P86		1.0435	1.0514	0.0030	0.0064	0.0078	0.0105	
B3PW91		1.0417	1.0494	0.0029	0.0069	0.0077	0.0107	
Q1		SCF	1.0629	1.0699	0.0027	0.0053	0.0069	0.0091
		MP2	1.0220	1.0293	0.0028	0.0058	0.0072	0.0097
	B3LYP	1.0374	1.0453	0.0030	0.0060	0.0078	0.0103	
	B3P86	1.0382	1.0459	0.0030	0.0064	0.0077	0.0104	
	B3PW91	1.0363	1.0440	0.0029	0.0068	0.0076	0.0106	
	Q2	SCF	1.0636	1.0706	0.0027	0.0053	0.0069	0.0092
MP2		1.0219	1.0292	0.0028	0.0058	0.0073	0.0097	
B3LYP		1.0381	1.0460	0.0030	0.0060	0.0078	0.0103	
B3P86		1.0389	1.0467	0.0030	0.0064	0.0077	0.0104	
B3PW91		1.0369	1.0446	0.0029	0.0068	0.0076	0.0106	
Q3		SCF	1.0636	1.0706	0.0027	0.0053	0.0069	0.0092
	MP2	1.0219	1.0292	0.0028	0.0058	0.0073	0.0097	

total dipole moment of the complex has been estimated at  $\mu(\text{H}_2\text{O})_2\text{He} = 1.0130 e a_0$ , which corresponds to an interaction dipole moment  $\mu_{\text{int}} = 0.0096 e a_0$ .

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