



Relative strength of hydrogen bond interaction in alcohol–water complexes

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Abstract

Hydrogen binding energies are calculated for the different isomers of 1:1 complexes of methanol, ethanol and water using ab initio methods from MP2 to CCSD(T). Zero-point energy vibration and counterpoise corrections are considered and electron correlation effects are analyzed. In methanol–water and ethanol–water the most stable heterodimer is the one where the water plays the role of proton donor. In methanol–ethanol the two isomers have essentially the same energy and no favorite heterodimer could be discerned. The interplay between the relative binding energy is briefly discussed in conjunction with the incomplete mixing of alcohol–water systems.

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1. Introduction

Alcohol–water mixtures are very important systems exhibiting properties that are of great interest in physics, chemistry and biology. These include several thermodynamic and physico-chemical properties [1–3]. For instance, the mixture of alcohol and water exhibits an entropy value that is smaller than expected [1]. This leads to the concept of negative excess entropy [1,4,5]. Most of these intriguing aspects are consequence of the great ability of both water and alcohol to make hydrogen bonds. Alcohol–water systems can have two hydrogen-bonded structures corresponding to the two possible heterodimers (or isomers) where alcohol is a proton acceptor, $\text{RHO} \cdots \text{H}_2\text{O}$, or a proton donor, $\text{ROH} \cdots \text{OH}_2$. The existence of these two isomers is very easy to understand but the relative strength of the two possible conformations is more difficult to ascertain.

Methanol–water, for instance, is one of the examples of this amphoteric relation where both methanol and water can act as proton donor and proton acceptor of hydrogen bonds. The question of which of the two isomers is more stable has been controversial [6–8]. It was not until very recently that the question has been confidently answered for the gas phase complexes. Detailed microwave rotation tunneling spectroscopy has established [9] that the complex where methanol is the proton acceptor and water is the proton donor, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, is the more stable isomer in gas phase. Theoretical calculations [10–12] have indeed confirmed the greater stability of this isomer but obtained a relative stability that is less than 1 kcal/mol.

Recent experimental studies have demonstrated that alcohol–water leads to incomplete mixing [4,5] and inferred [4] that the negative entropy mixing of alcohol–water mixtures arises from the interplay between the relative strengths of the alcohol–alcohol, alcohol–water and water–water hydrogen bonds. Therefore, there is considerable interest in the theoretical determi-

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nation of the relative binding energies of heterodimers. Of course, there are a considerable number of works dedicated to the study of the structure and binding energy of some alcohol–water complexes using several theoretical models [13–23]. To obtain the relative binding energies, free from the artifact of different approximations, it is imperative to have the same high-level theoretical model for all heterodimers of interest. In this work we address to this issue and use high-level *ab initio* calculations to study the relative binding energy of the 1:1 complexes obtained from water, methanol and ethanol. These include the heterodimers obtained from water–methanol, water–ethanol and methanol–ethanol and the dimers of water, methanol and ethanol. Ethanol is known to exist in two forms, the *trans* and *gauche*. In the case of water–ethanol and ethanol–water we have considered both the *trans* and *gauche* configurations of ethanol. In total, eleven different complexes are obtained and their relative binding energies are systematically compared and the role of electron correlation effects analyzed.

2. Calculation details

Second-order Møller–Plesset MP2/aug-cc-pVDZ [24] calculations were performed to obtain the geometries of the complexes involving water, methanol and ethanol. Full geometry optimization is performed for the dimers $(\text{H}_2\text{O})_2$, $(\text{CH}_3\text{OH})_2$ and $(\text{CH}_3\text{CH}_2\text{OH})_2$, and the heterodimers $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}\cdots\text{OH}_2$; $\text{CH}_3\text{CH}_2\text{HO}\cdots\text{H}_2\text{O}$ and $\text{CH}_3\text{CH}_2\text{OH}\cdots\text{OH}_2$; $\text{CH}_3\text{CH}_2\text{HO}\cdots\text{HOCH}_3$ and $\text{CH}_3\text{CH}_2\text{OH}\cdots\text{OHCH}_3$. To abbreviate these different isomers we adopt the notation that the DA acronym stands for the proton donor and proton acceptor of the hydrogen bond. For instance, MW stands for the $\text{CH}_3\text{OH}\cdots\text{OH}_2$ isomer. The *gauche* form of ethanol is represented by E_g , otherwise the *trans* form is assumed. Figs. 1–3 show the results for the hydrogen bond distances of these optimized clusters. Using these optimized structures, binding energies, dipole moment and rotational constants were obtained for all these complexes. Analysis of the vibration frequencies was made to ensure that the calculated structures are true minima of the energy surfaces and to obtain the

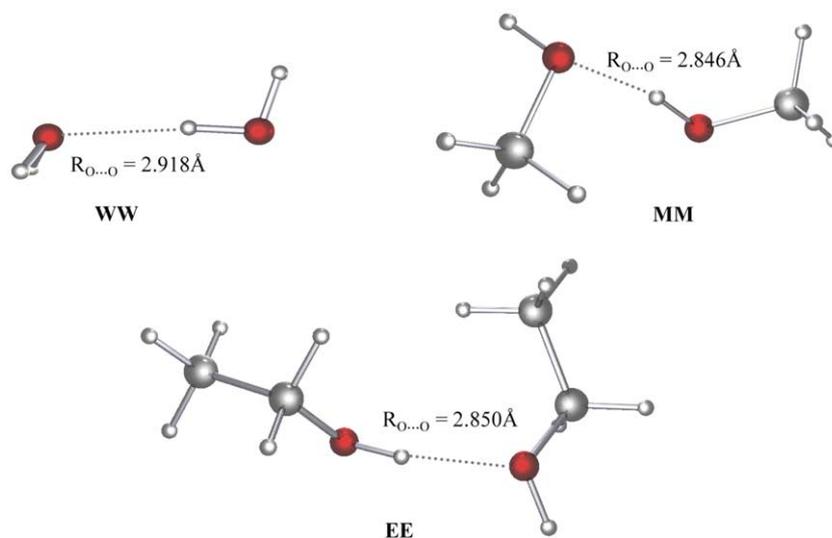


Fig. 1. The MP2/aug-cc-pVDZ optimized structures for the hydrogen bond dimers: water (WW), methanol (MM) and ethanol (EE). The calculated hydrogen bond distances $R_{\text{O}\cdots\text{O}}$ are shown.

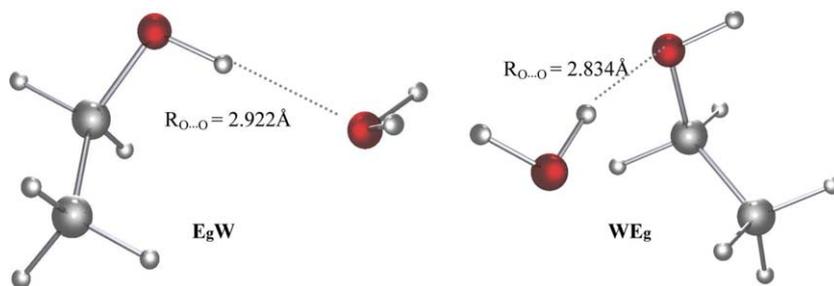


Fig. 2. The MP2/aug-cc-pVDZ optimized structures of the heterodimer complexes involving *gauche* ethanol and water ($E_g\text{W}$ and WE_g). The acronym DA stands for proton donor and acceptor, respectively. The calculated distances $R_{\text{O}\cdots\text{O}}$ are shown.

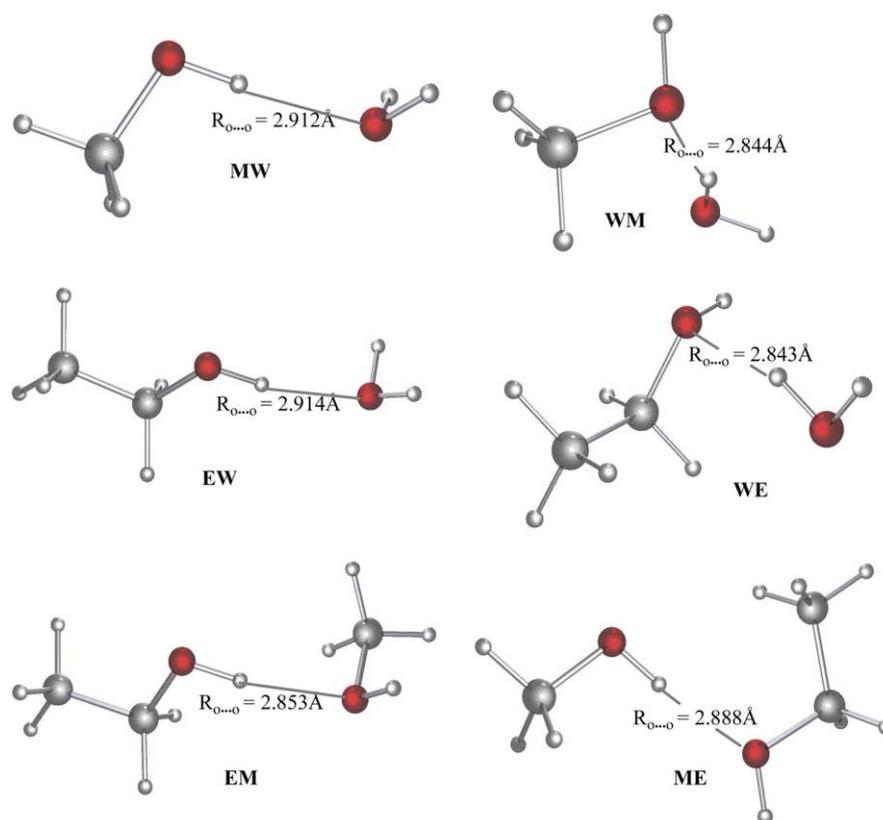


Fig. 3. The MP2/aug-cc-pVDZ optimized structures of the heterodimer complexes involving methanol and water (MW and WM); ethanol and water (EW and WE); and methanol and ethanol (ME and EM). We use the acronym DA for proton donor and acceptor, respectively. The calculated distances $R_{O\dots O}$ are shown.

zero-point vibration energies. To analyze the role of the electron correlation effects on the relative stabilities of the different heterodimers single-point Coupled-Cluster [25] calculations were performed at the CCSD(T) and full-fourth-order MP4 [26] levels. As it is conventional, correction to the basis set superposition error (BSSE) is obtained for the binding energies using the counterpoise correction [27]. There has been, however, suggestions [28] that in some cases counterpoise correction may not be advised. All calculations were carried out with the GAUSSIAN 98 ab initio package [29].

3. Results and discussion

Figs. 1–3 show all the systems considered here and give the optimized hydrogen bond distances. These are summarized in Table 1 that also shows the calculated dipole moments and rotational constants.

Overall the calculated hydrogen bond distances are in good agreement with previous available theoretical results, when available [10,11,15,16,18,21,30]. The calculated dipole moments are in very good agreement with experimentally known results for the isolated molecules. For water and methanol, the results of 1.88 and 1.71 D

Table 1
Calculated hydrogen bond distances $R_{O\dots O}$ and $R_{O\dots H}$ (Å), dipole moment (Debye) and rotational constants (GHz) for the monomers and heterodimers

	$R_{O\dots O}$	$R_{O\dots H}$	μ	I_A	I_B	I_C
<i>Monomer</i>						
H ₂ O (W)	–	–	1.879	796.37	433.47	280.69
Methanol (M)	–	–	1.714	126.02	24.36	23.51
Ethanol (E)	–	–	1.624	34.42	9.33	8.10
Ethanol (E _g)			1.756	33.93	9.09	8.03
<i>Dimer</i>						
WW	2.918	1.951	2.640	213.86	6.38	6.38
MM	2.846	1.887	2.499	16.05	2.39	2.31
EE	2.850	1.885	2.593	6.13	1.21	1.10
<i>Heterodimer</i>						
WM	2.844	1.904	2.040	24.92	4.62	4.05
MW	2.912	1.942	2.734	31.96	3.80	3.53
EW	2.914	1.951	2.494	26.56	2.05	1.97
WE	2.843	1.900	1.944	8.97	3.55	2.85
E _g W	2.922	1.949	2.839	9.61	3.05	2.51
WE _g	2.834	1.890	2.044	8.69	3.69	2.88
ME	2.888	1.919	3.323	8.50	1.75	1.50
EM	2.853	1.986	2.664	12.10	1.46	1.43

All results are obtained using the MP2/aug-cc-pVDZ optimized geometries.

are in good agreement with the experimental results of 1.86 and 1.70 D, respectively. For ethanol, the average experimental result is 1.69 D [31]. Upon hydrogen bond formation the combined dipole moment of ME has the largest value whereas the combined WE has the smallest. In the first case there is a large parallel component whereas in the latter there is a large anti-parallel component of the separate dipole moments as it can be seen in Fig. 3.

Before proceeding it is convenient to consider the *trans* and *gauche* forms of ethanol. Table 2 presents the total energies of ethanol in the *trans* and *gauche* forms. Using all theoretical models considered here the *trans* form is more stable than the *gauche* form, but the relative energy is very small in agreement with previous studies [14,32]. At the highest correlation level, CCSD(T), the difference is only 0.16 kcal/mol, in very good agreement with the result of 0.14 kcal/mol obtained in [14] using density functional theory. When ethanol is hydrogen bonded to water the difference in relative energy for the *trans* and *gauche* heterodimers is considerably smaller. Taking the MP2 level and considering the vibration zero point energy the difference

is essentially null. The total energy of the water–ethanol system is the same whether the ethanol is in the *trans* or *gauche* form. A more delicate situation is involved when considering the ethanol dimer because of the large variety of conformers [14,33]. Recent investigations have shown that these conformers have equivalent binding energies. For instance, the *trans*–*gauche* differs from the *trans*–*trans* by less than 0.06 kcal/mol [14]. The *gauche*–*gauche* has a larger difference but still less than 0.3 kcal/mol. Explicit consideration of all possible conformers of the ethanol dimer would depart us from the present focus of interest. In the following we consider the ethanol dimer only in the *trans*–*trans* form.

Table 3 gives the calculated binding energies of all eleven hydrogen-bonded systems considered here and it allows a systematic analysis of the relative strengths of the different isomers. Note that for the ethanol–water case we find that the water donor heterodimer is more stable by the same amount regardless whether one is considering the *gauche* or the *trans* form. For instance, at the MP2 level, considering zero point vibration correction, the relative stability is 0.71 kcal/mol for both the *trans* and *gauche* forms. The CCSD(T) and the

Table 2

Total (in hartree) and relative (in kcal/mol) energies of the heterodimers of ethanol (*trans* and *gauche*) and water

Method	Ethanol (<i>t</i>)	Ethanol (<i>g</i>)	$\Delta(t - g)$	WE_t	WE_g	$\Delta(tg)$	E_tW	E_gW	$\Delta(tg)$
MP2	-154.6138168	-154.6134132	-0.25	-230.8854660	-230.8855302	0.04	-230.8829932	-230.8831952	0.13
MP3	-154.6430265	-154.6427844	-0.15	-230.9185886	-230.9187749	0.12	-230.9166726	-230.9169186	0.15
D-MP4	-154.6550447	-154.6547702	-0.17	-230.9346244	-230.9347633	0.09	-230.9326387	-230.9328562	0.14
DQ-MP4	-154.6461873	-154.6458418	-0.22	-230.9228668	-230.9229440	0.05	-230.920969	-230.9211134	0.09
SDQ-MP4	-154.650142	-154.6498259	-0.20	-230.9288678	-230.9289611	0.06	-230.9268192	-230.9270091	0.12
MP4	-154.6662887	-154.6660202	-0.17	-230.9516194	-230.9517403	0.08	-230.9492452	-230.9495416	0.19
CCSD	-154.6499184	-154.6495985	-0.20	-230.9283676	-230.9284528	0.05	-230.9263727	-230.9265515	0.11
CCSD(T)	-154.6661319	-154.6658739	-0.16	-230.9507304	-230.9508539	0.08	-230.9484605	-230.9487488	0.18
MP2 + ZPE			-0.21				-0.01		0.05

The acronym DA stands for proton acceptor and donor, respectively. E_g stands for the *gauche* form of ethanol. All calculations are made using the MP2/aug-cc-pVDZ optimized geometry. ΔZPE stands for zero point energy difference obtained using MP2/aug-cc-pVDZ.

Table 3

Calculated counterpoise corrected binding energies (kcal/mol) of the heterodimer complexes

Method	WW	MM	EE	WM	MW	WE	EW	WE_g	E_gW	ME	EM
MP2	4.46	5.22	5.69	5.15	4.48	5.49	4.27	5.78	4.53	5.15	5.08
MP3	4.39	4.96	5.34	4.90	4.40	5.18	4.21	5.46	4.40	4.91	4.83
D-MP4	4.31	4.88	5.25	4.82	4.32	5.10	4.13	5.37	4.33	4.83	4.75
DQ-MP4	4.20	4.69	4.96	4.67	4.17	4.92	3.96	5.19	4.17	4.63	4.53
SDQ-MP4	4.23	4.80	5.14	4.76	4.22	5.03	4.03	5.30	4.24	4.74	4.66
MP4	4.39	5.14	5.68	5.04	4.44	5.38	4.27	5.65	4.50	5.11	5.06
CCSD	4.23	4.77	5.09	4.74	4.22	5.01	4.02	5.27	4.23	4.70	4.63
CCSD(T)	4.41	5.11	5.62	5.02	4.45	5.35	4.28	5.62	4.50	5.06	5.02
ΔZPE	2.11	1.29	1.24	1.94	1.58	1.96	1.45	2.01	1.53	1.18	0.93
MP2 + ΔZPE	2.35	3.93	4.45	3.21	2.90	3.53	2.82	3.77	3.04	3.97	4.15

The acronym DA stands for proton acceptor and donor, respectively. E_g stands for the *gauche* form of ethanol. All calculations are made using the MP2/aug-cc-pVDZ optimized geometry. ΔZPE stands for zero point energy difference between the complex and the separate parts obtained using MP2/aug-cc-pVDZ.

intermediate MP3 and MP4 results give a clear picture of the role of electron correlation effects on the relative binding energies. The basis set limit estimated for the methanol dimer at the MP2 level [18] is 5.58 kcal/mol. Our MP2 result for the methanol dimer is lower than this basis set limit by ca. 0.4 kcal/mol. At all levels of calculations considered in this work the ethanol dimer is the strongest bond system. MP2 calculations at the HF optimized geometry [22] has found that the binding energy in the ethanol dimer is stronger than the methanol dimer by 0.5–0.8 kcal/mol. Our results for the *trans-trans* form are consistent with this picture giving more stability to the ethanol dimer by a value of 0.5 kcal/mol using MP2 and CCSD(T).

We now consider the alcohol–water heterodimers. The results for the MW and WM isomers are similar to the ones obtained before and are consistent in that the WM isomer is more strongly bound than MW by less than 1 kcal/mol [9–11]. At the MP2 level we find that WM is more stable than MW by 0.7 kcal/mol. This is the same energy difference obtained using the B3LYP model [10], in spite of the fact that the individual binding energies using DFT are slightly higher. This relative energy value decreases to only 0.3 kcal/mol if the difference in zero point energy vibrations is taken into account. Now we analyze the results for the ethanol–water system. The WE–EW (or WE_g-E_gW) heterodimer difference is the largest difference found among the possible heterodimers considered here. In the cases of alcohol–water mixtures, methanol–water and ethanol–water, it is found that the most stable heterodimer has the alcohol as the proton acceptor and water as the proton donor. But in the case of ethanol the energy difference between the two stable heterodimers is more sizable. The methanol–ethanol system has been more scarcely studied. It is obtained here that these isomers have binding energies of 5.15 kcal/mol (ME) and 5.08 kcal/mol (EM) at the second-order MP2 level. We are not aware of any recent theoretical estimate of these binding energies. Here, the ME is found to be more stable than EM by a negligible amount of less than 0.1 kcal/mol in all theoretical models considered here, from MP2 to CCSD(T). Including the difference in zero-point energy vibrations the relative stability, in turn, favors the EM heterodimer by 0.2 kcal/mol. Hence the methanol–ethanol heterodimers have essentially the same binding energy with no indication of a preferred isomer. It can be noted that the relative stability of the different isomers reflects closely the trend of the calculated hydrogen bond distances, as seen in Figs. 2 and 3.

In all the results it is verified that the role of electron correlation effects beyond MP2 are not very important in defining the relative strengths of the different heterodimers. This is not the same as stating that electron correlation effects in hydrogen binding energies are not important but rather that MP2 gives balanced results

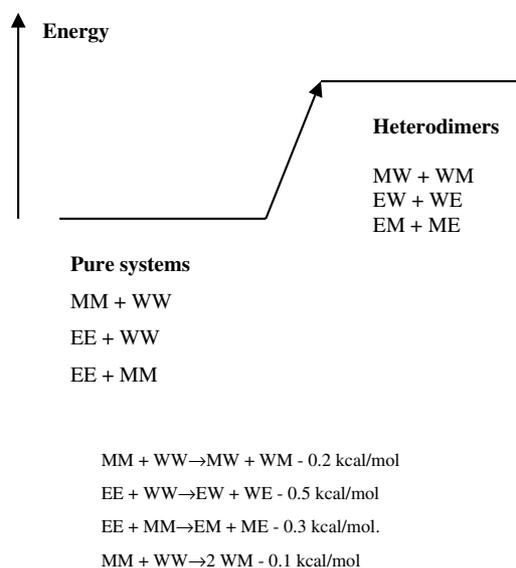


Fig. 4. Relative strengths of homogeneous and mixed systems.

[34,35]. In the present systems high-order electron correlation effect is systematic but small. High-level electron correlation, i.e. beyond MP2, in no case considered here gives a different pattern of the relative binding energies of the two possible heterodimers.

An important theoretical information to rationalize liquid mixtures is the energetic involved in making and breaking hydrogen bonds. It has been discussed that methanol–water leads to incomplete mixtures at the microscopic level and this relates to the negative entropy value associated to alcohol–water mixtures [4,5]. Using the MP2 results with zero-point energy corrections extracted from Table 3 it is seen that breaking the methanol–methanol hydrogen bond to form either MW or WM decreases the stability by ca. 1.0 kcal/mol. The breaking of two hydrogen bonds such as in MM and WW to form MW and WM ($MM + WW \rightarrow MW + WM$) is calculated to be unfavorable by less than 0.2 kcal/mol, with the MP2 results corrected for zero-point energy differences. This energetic cost is of course very small. Fig. 4 illustrates some of the relative strengths of the hydrogen bonds obtained here. The small energy differences may explain in part the incomplete mixing in terms of similar relative stabilities. The situation found in a liquid is not the same as that in geometry-optimized complexes but the energies of the methanol–water heterodimers are equivalent also in the liquid case [12].

4. Summary and conclusions

Hydrogen binding energies are calculated for two common alcohol and water mixtures using highly correlated methods varying from second-order MP2 to

CCSD(T) levels. We find that in the case of methanol–water and ethanol–water the most stable heterodimer is the one where the water plays the role of proton donor. For methanol the relative stability is found to be less than 1.0 kcal/mol in agreement with previous calculations. In the case of ethanol, either the *trans* or *gauche* forms, the difference is larger than 1.0 kcal/mol. The role played by electron correlation effects beyond second-order MP2 has no influence in the relative stability of the heterodimers. In the case of the methanol–ethanol mixture the counterpoise corrected hydrogen binding energies at the second-order MP2 are 5.15 and 5.08 kcal/mol, for the case where methanol is the proton donor and proton acceptor, respectively. These two isomers are found to have essentially the same energy in all theoretical models considered and no favorite isomer could be discerned. The interplay between these relative energy differences is briefly discussed in possible conjunction with the incomplete mixture of alcohol–water systems.

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