

Theoretical analysis of the hydrogen bond interaction between acetone and water

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Abstract

The hydrogen bond interaction between acetone and water is investigated at the ab initio MBPT/CC levels using different approximations and basis sets. At the highest level the binding energy is obtained as $5.6 \text{ kcal mol}^{-1}$. Analysis of the electron correlation effects shows only a very mild influence on the binding energy. Study of the blue shift of the $n \rightarrow \pi^*$ transition of acetone in water shows that the hydrogen bond has a great contribution to the total shift. The use of the geometry optimized acetone–water cluster gives results in excellent but unrealistic agreement with the experimental result. The adequacy of using cluster structures and cluster models for studying solvent effects is analyzed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio; Acetone; Hydrogen-bond; Solvent shifts; Spectrum

1. Introduction

Hydrogen bonding is a topic of considerable interest in physics, chemistry and biology [1]. It lies at the heart of a series of phenomena ranging from the structure of liquid water, hydrophobic phenomena and cluster physical-chemistry. The nature of hydrogen bonding interaction has evolved from a pure electrostatic model [2] to more sophisticated models involving dispersion interaction [3–5].

In more recent years there has been a great increase in the study of solvent effects in both structure and spectroscopy of hydrogen bonded systems [6–11]. One example is the solvent effect of the $n \rightarrow \pi^*$ absorption transition of acetone in water [12–18]. It

is known experimentally [19,20] that this first absorption transition suffers a blue shift of about 1560 cm^{-1} in water, as compared to the isolated gas phase. Although there has been some successful theoretical treatments [12–18] of this blue shift, a detailed analysis of the hydrogen bond interaction known to exist between acetone and water, is still lacking.

In this paper we discuss the structure and bonding of the acetone–water complex as obtained by high-level ab initio calculations. We thus report geometry optimization and calculated binding energies between acetone and water for a variety of theoretical models and basis sets. The role of basis set size, electron correlation and basis set superposition effects are analyzed in detail. The energetically more stable structure found for this complex is not entirely new and in fact it has been obtained previously [21–23] either by explicit calculations or simply inferred from results on the similar formaldehyde–water complex [24–26]. However, in this paper we put forward

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what we believe are now the most accurate results for the hydrogen bond interaction between acetone and water, as obtained from high-level calculations and systematic analysis of the theoretical results obtained.

In the second part we pay some attention to the influence of the hydrogen bond to the solvatochromic shift of the $n \rightarrow \pi^*$ absorption transition of acetone in water.

2. Methods of calculations

Geometry optimization of the acetone–water complex has been performed initially at the Hartree–Fock (SCF) level of calculation using a variety of basis sets. SCF calculations on hydrogen bonded systems have been largely performed in the recent past. In this theoretical model the electrostatic, exchange and some induction–polarization effects are included. In more recent years it has been learnt that the induced–induced dispersion interaction may be of great importance [3–5]. It is therefore necessary to go beyond the SCF model and include some of the correlation effects. Therefore our geometry optimizations are performed also at the second-order many-body perturbation theory, MBPT(2) best known as second-order Möller–Plessett theory, MP2. For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis set. We thus analyze the separate influence of diffuse and polarization functions as well as the role played by electron correlation effects. In more complex systems the use of large basis sets becomes prohibitive. In fact it is clear that in hydrogen bonded systems the atoms involved in the bond are much more sensitive to the basis set, in particular regarding the use of diffuse and polarization functions. We would like to analyze the performance of an intermediate basis set. Thus a selective basis set consisting of a total 116 contracted gaussian-type orbitals has also been used. This is obtained from the 6-311++G** basis set (C,O:5s4p1d/H:4s1p) but stripping out some of the diffuse or polarization functions of the peripheral atoms. For the methyl groups we used a 4s3p basis on the C atom and 3s on the H atoms. For the carbonyl we have used 4s3p1d on C and 5s4p1d on the O. These include both diffuse and polarization functions. For the water molecule we

used a 4s3p1d basis on the O atom and 4s1p basis on the H atom, again including diffuse and polarization functions. This differential treatment emphasizes the atoms more involved in the complex binding and still keeps the size of the basis set within a treatable size. This basis set will be referred to as intermediate basis set and the results obtained will be compared with the results obtained with the 6-311++G* results.

After obtaining these optimized structures, single-point calculations are performed with a variety of size-extensive theoretical models [27–29]. These include MP3 and MP4 as well as the more sophisticated coupled-cluster models such as CCSD and CCSD(T). This latter model CCSD(T) [29], should be considered as the most reliable theoretical model of this study. The calculated binding energies obtained with all the above theoretical procedures are then corrected for the basis set superposition error (BSSE) [30]. This is done using the counterpoise method [31]. Finally, all calculations are performed using the GAUSSIAN/92 program [32].

3. Results and discussion

The Fig. 1 shows the two favored structures of the hydrogen bond between water and acetone. These two are also the most frequent dimer structure appearing in Monte Carlo simulation of acetone in water [33]. The collinear structure is not a true minimum of the entire potential energy hypersurface. However it is a frequent structure appearing in the liquid at room temperature. Table 1 shows the optimized geometries of these structures and compares with different theoretical models and includes the results obtained for the isolated moieties. Only the results obtained starting from the MP2/3-21+G level are shown. Those obtained at lower level and smaller basis sets are similar to the ones obtained in [21]. Several aspects emerge from the results shown in Table 1. First we note that the hydrogen bond is longer for the collinear than for the bent structure. With the best basis set the SCF/6-311++G* result is as large as 2.04 Å. Inclusion of electron correlation effects decreases this value. At the best MP2/6-311++G* level the hydrogen bond distance is found to be 1.96 Å. As a comparison the equivalent result with the intermediate basis

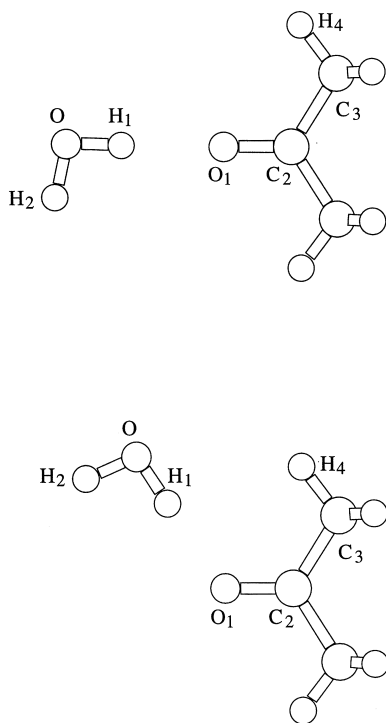


Fig. 1. The two structures of acetone–water complex. The top shows the ‘collinear’ and the bottom shows the ‘bent’ structures. Atomic numbering is used to define the geometrical parameters.

gives the value of 1.93 Å. It is interesting to note that the hydrogen bond distance is the same with the MP2/6-311++G* and MP2/6-311G models. Comparison with the results obtained with the MP2/6-311+G and MP2/6-311++G models shows that the equivalence between the MP2/6-311++G* and MP2/6-311G models is due to a cancellation effect between diffuse and polarization functions. This is valid only for the hydrogen bond distance. Considering all geometric parameters the results obtained with the MP2/6-311++G* models is similar to those obtained with the MP2/intermediate. This suggests the use of a compromising basis set for larger hydrogen bonded complexes. It is interesting to note that the hydrogen bond increases the carbonyl C=O distance for the bent structure and slightly decreases for the collinear one. This is followed by an increase of the OH distance involved in the bond. This C=O distance variation has an effect on the $n \rightarrow \pi^*$ absorption band of acetone. Indeed, as noted previously [26] an increase (decrease) of the C=O distance leads to a red (blue)

shift of the $n \rightarrow \pi^*$ absorption band of acetone as compared to gas phase. This red shift is opposite to the shift observed experimentally known to be a blue shift of 1560 cm^{-1} . Thus the C=O lengthening obtained with the hydrogen bond gives a structural contribution to the solvatochromism that is in the opposite direction (red) to that observed experimentally (blue). Fig. 2 illustrates the effect on the $n \rightarrow \pi^*$ transition of acetone with the C=O distance variation. The C=O lengthening is the only appreciable change in geometry after the binding. For the water, the OH involved in the bond is increased whereas the other OH is essentially unaltered. The HOH angle is slightly increased after the hydrogen bond formation.

In every theoretical model considered the bent structure is found to be energetically lower (by less than 2 kcal mol^{-1}). This small energy difference between these two structures can be interpreted as the result of two opposite and competing effects. One is the dipole–dipole interaction that favors the collinear structure. The other is the directional character of the sp^2 hybridization of the lone pair of the oxygen at the C=O end.

To analyze in more detail the role of basis set size and electron correlation effects on the binding energy between acetone and water we use Table 2. The BSSE is corrected using the counterpoise method of Boys and Bernardi [31]. All numbers given for the binding energies in Table 2 were obtained using this procedure. The numbers shown in parenthesis are not corrected for BSSE and were obtained using the geometries optimized for the separate moieties. Thus the difference in the numbers with and without counterpoise correction includes also some structural relaxation. This table gives a detailed analysis of the binding energy obtained with several different theoretical models. Generally, electron correction effects slightly decrease the calculated binding energy. However, the numbers are not very sensitive after MP2. The results of Table 2 clearly show that the effects of electron correlation are very mild on the calculated acetone–water binding energy. Thus high-order electron correlations effects are found to be far less important than the basis set influence or the magnitude of BSSE. The results obtained with the larger basis sets show that the most accurate values given by CCSD(T) are in fact similar to those obtained at second-order MP2. The intermediate

Table 1

The optimized geometry of the acetone–water cluster in comparison with the isolated moieties using different theoretical models. Distances in Å, angle in degrees. Collinear and bent structures correspond to the top and bottom structures of Fig. 1. See text

		O ₁ C ₂	C ₂ C ₃	C ₃ H ₄	O ₁ C ₂ C ₃	C ₂ C ₃ H ₄	OH ₁	OH ₂	H ₁ OH ₂	H ₁ O ₁	H ₁ O ₁ C ₂
MP2/3-21+G	Collinear	1.269	1.521	1.093	121.4	109.7	0.992	0.989	109.6	1.875	180.0
	Bent	1.273	1.521	1.093	121.3	110.1	1.000	0.987	111.4	1.860	117.7
	Isolated	1.269	1.524	1.093	121.7	109.5	0.989	0.989	109.4	—	—
MP2/6-311G	Collinear	1.259	1.514	1.091	120.9	109.2	0.971	0.968	110.0	1.987	180.0
	Bent	1.264	1.513	1.091	120.9	109.7	0.976	0.967	111.6	1.961	116.7
	Isolated	1.260	1.516	1.092	121.1	109.0	0.969	0.969	109.9	—	—
MP2/6-311+G	Collinear	1.261	1.513	1.092	121.0	109.5	0.976	0.970	111.1	1.964	180.0
	Bent	1.264	1.512	1.092	121.0	110.1	0.980	0.970	112.2	1.918	119.2
	Isolated	1.261	1.515	1.092	121.2	110.4	0.971	0.971	111.1	—	—
SCF/6-311++G	Bent	1.222	1.501	1.077	121.0	110.4	0.954	0.945	113.2	1.927	123.7
	Isolated	1.217	1.502	1.077	121.2	110.0	0.946	0.946	112.6	—	—
MP2/6-311++G	Bent	1.264	1.512	1.092	121.0	109.9	0.980	0.970	112.0	1.921	119.6
	Isolated	1.261	1.515	1.092	121.2	109.3	0.971	0.971	111.2	—	—
SCF/6-311++G*	Bent	1.193	1.511	1.086	121.6	110.5	0.945	0.940	108.4	2.036	124.0
	Isolated	1.188	1.513	1.080	121.7	110.1	0.940	0.940	108.2	—	—
MP2/6-311++G*	Bent	1.226	1.511	1.094	122.2	111.0	0.967	0.959	108.0	1.961	118.0
	Isolated	1.221	1.515	1.094	121.8	109.9	0.959	0.959	107.6	—	—
SCF/intermediate	Bent	1.192	1.509	1.084	121.4	110.2	0.945	0.941	105.1	2.028	129.2
	Isolated	1.187	1.511	1.078	121.6	110.0	0.941	0.941	105.5	—	—
MP2/intermediate	Bent	1.225	1.509	1.092	121.2	109.8	0.964	0.957	102.9	1.933	117.8
	Isolated	1.221	1.512	1.092	121.4	109.3	0.958	0.958	102.4	—	—

values are however instructive. For this matter let us consider the results obtained with the larger 6-311++G* basis set (the right most column of Table 2). The MP4 result differs from SCF by $-0.04 \text{ kcal mol}^{-1}$ and MP2 by only $-0.16 \text{ kcal mol}^{-1}$. The difference between MP4 and SDQ-MP4 shows that the effects of triple excitation in fourth-order is only $0.05 \text{ kcal mol}^{-1}$. The difference between CCSD and MP4 that gives the contribution of high-order single and double excitations amounts to $-0.04 \text{ kcal mol}^{-1}$. These clearly indicate that high-order correlation effects are mild. In fact, the difference between CCSD(T) and SCF amounts to a negligible $0.02 \text{ kcal mol}^{-1}$. As it can be seen the same numerical analysis holds for the results obtained with the intermediate basis set. Hence, as far as the binding energy is involved the acetone–water complex is insensitive to electron correlation effects, or more specifically the dispersion forces do not play a significant role. The difference in binding energy obtained by CCD or DQ-MP4 and SCF (including the counterpoise correction) is a relatively good measure of the dispersion contribution. For the 6-311++G* basis obtained using the MP2/6-311++G* geometry our estimate of

the dispersion contribution to the hydrogen binding is $0.1 \text{ kcal mol}^{-1}$. As a complement Table 3 shows the calculated total energies for the acetone–water complex using the largest basis sets. The structural results obtained here for the acetone–water complex are in good agreement with those obtained by Liao et al. [23]. Our best result for the hydrogen bond distance is 1.961 Å and it also shows that the OH distance of

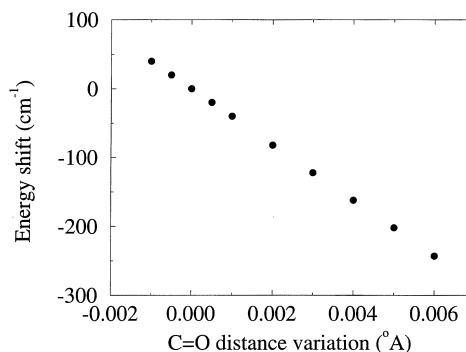


Fig. 2. Variation of the $n \rightarrow \pi^*$ absorption transition of isolated acetone with the C=O distance variation. Numerical values obtained with CIS/6-311G.

Table 2

Effects of electron correlation and basis set size on the binding energy of the water–acetone complex (kcal mol⁻¹). Results without correction for basis set superposition are in parenthesis. In each case the corresponding optimized geometries are used and given at the bottom

	6-311G	6-311+G	Intermediate	Intermediate	6-311++G*
SCF	6.86 (8.00)	7.17 (7.52)	5.22 (5.58)	4.57 (5.50)	5.54 (5.59)
MP2	5.63 (8.50)	6.25 (7.84)	5.13 (7.03)	4.54 (7.08)	5.66 (7.17)
MP3	5.88 (8.23)	6.44 (7.88)	5.26 (6.79)	4.65 (6.85)	5.71 (7.03)
DQ-MP4	5.54 (8.02)	6.11 (7.56)	4.94 (6.50)	4.35 (6.58)	5.42 (6.77)
SDQ-MP4	5.59 (8.32)	6.22 (7.76)	4.97 (6.67)	4.37 (6.74)	5.45 (6.84)
MP4	5.62 (8.62)	6.31 (8.03)	5.01 (6.98)	4.42 (7.05)	5.50 (7.11)
CCSD	5.61 (8.25)	6.24 (7.72)	5.02 (6.66)	4.42 (6.73)	5.46 (6.81)
CCSD(T)	5.70 (8.53)	6.38 (8.02)	5.12 (6.97)	4.52 (7.03)	5.56 (7.09)
#CGTO	89	109	116	116	143
Geometry	MP2	MP2	MP2	MP2	MP2
	6-311G	6-311G	6-311G	Intermediate	6-311++G*

the water increases by 0.01 Å. As to the binding energy we find their [23] result to be slightly underestimated. At the best level CCSD(T)/MP2-6311++G* we obtain a binding energy of 5.6 kcal mol⁻¹, as compared to their estimated best result of 3.7 kcal mol⁻¹. Our lowest result for the binding energy is obtained using the intermediate basis set (4.5 kcal mol⁻¹). Both studies agree that the binding energy is more sensitive to the basis sets than to the correlation effects.

Finally, we comment on the influence of the hydrogen bond interaction between acetone and water to the solvent shift of the $n \rightarrow \pi^*$ transition of acetone in water as compared to isolated acetone. This solvatochromic shift has been studied before [12–18]. Using the self-consistent reaction field it has been recognized [12–14] the need to include the acetone–water complex in the cavity. However, there still seems to lack an ab initio analysis of the separate

influence of the hydrogen bond to the solvatochromic shift. In the case of formaldehyde in water it has been suggested [18] that the first solvation shell is responsible for 50% of the blue shift of the $n \rightarrow \pi^*$ transition of formaldehyde in water. In contrast to the case of formaldehyde where the experimental data is only inferred, in the case of acetone the experimental blue shift of 1560 cm⁻¹ is well documented [19,20]. Using several of the optimized structures of Table 1 and several basis sets we have performed calculations of the $n \rightarrow \pi^*$ absorption transition in isolated acetone and in the acetone–water complex. As only size-extensive method should be used to avoid artificial size effects we used the single-excited configuration interaction (CIS) method. As it is well known this method gives transition energies that are usually larger than experimental. However as we are looking only at the lowest transition and, in fact, only the difference between the two $n \rightarrow \pi^*$ transition in the

Table 3

Results for the total energies (in a.u.) of the acetone–water complex using different levels and basis sets at the corresponding optimized (MP2 level) geometries

Level	6-311+G	Intermediate	6-311++G*
SCF	–267.9465713	–268.0321747	–268.0521862
MP2	–268.5297132	–268.7794499	–268.8687400
MP3	–268.5353826	–268.7998759	–268.8924137
DQ-MP4	–268.5515210	–268.8089307	–268.9000277
SDQ-MP4	–268.5637087	–268.8184133	–268.9107314
MP4	–268.5870608	–268.8455839	–268.9404517
CCSD	–268.5638934	–268.8186887	–268.9095860
CCSD(T)	–268.5851611	–268.8442434	–268.9374815

Table 4

The calculated solvatochromic shift of the ($n \rightarrow \pi^*$) absorption band of acetone in water compared to the gas phase (ΔE in cm^{-1}). The solvatochromic shift $\langle \Delta E \rangle$ is averaged over the MC configurations. In the case of the cluster only the ab initio optimized structure of Table 1 is used. See text

Geometry	System	Basis Set	$\langle \Delta E \rangle$
MP2/6-311++G*	$(\text{CH}_3)_2\text{CO} + \text{H}_2\text{O}^a$	6-311++G*	1530
		6-311+G*	1530
		6-311++G	1630
		6-311+G	1630
		6-311G	1650
MC liquid	$(\text{CH}_3)_2\text{CO} + \text{H}_2\text{O}^b$	6-311++G*	850 ± 80
		6-311G	980 ± 80
		3-21G	1010 ± 80
MC liquid	$(\text{CH}_3)_2\text{CO} + 2\text{H}_2\text{O}^b$	6-311++G*	1150 ± 120
		3-21G	1360 ± 120

^a Bent Structure.

^b Calculated using structures obtained from MC simulation.

monomer and in the complex the results should not be so much affected.

The Table 4 shows the spectral shift of the $n \rightarrow \pi^*$ transition of acetone due to the hydrogen bond using the optimized cluster structures previously obtained. With the geometry obtained with the MP2/6-311++G* method the transition shift varies from 1530 to 1650 cm^{-1} . The result for the CIS/6-311++G* is 1530 cm^{-1} , in excellent agreement with the experimental result of 1560 cm^{-1} . However, we are calculating the blue shift of the dimer complex and in this case the single water is free from hydrogen binding with other water molecules which is the real liquid situation. Thus we should consider the acetone–water complex as ‘extracted’ from the liquid. This is possible using the liquid structures generated by a Monte Carlo simulation of one acetone surrounded by 343 water molecules at $T = 298$ K. The quantum mechanical calculations are made using only the acetone and the corresponding hydrogen bonded water molecule of the acetone–water simulation [33]. In this case the calculated blue shift using the same CIS model drops by ~ 700 cm^{-1} giving a solvatochromic shift of 850 cm^{-1} . This number is obtained after (ensemble) averaging of many structures generated in the simulation. Only statistically uncorrelated structures [34] are used. In total 30 different CI calculations are made to obtain the average. The decrease in the transition energy shift in going from the cluster to the liquid is due to two

dominant factors. One is that in the cluster the acetone–water binding is stronger than in the liquid as in this case the water is also bound to other water molecules. Another aspect is that in the liquid there are several structures possible (including the collinear structure previously discussed) at a given temperature and not only a minimum-energy as in the case of the optimized cluster. The result of 850 cm^{-1} for the $n \rightarrow \pi^*$ shift due to the single water molecule corresponds to around 55% of the total solvatochromic shift of 1560 cm^{-1} . Table 4 summarizes these results and shows also the influence of a second hydrogen-bonded water molecule. The step-by-step influence of the first (water) neighbors is of major interest. Here our results indicate that the two hydrogen-bonded water molecules can account for nearly 70% of the total shift. Using geometry-optimized cluster will clearly overestimate the solvatochromic shift. The result obtained with the CIS/6-311++G* using the structures generated by the Monte Carlo simulation suggests that the first hydrogen bond contribution to the total solvatochromic shift of the $n \rightarrow \pi^*$ transition is around 55%. This is in agreement with previous studies [18,26] that indicate that long-range solvent effects are important. Inclusion of the second water molecule that also binds to acetone gives a total solvatochromism of around 70%. Although the acetone can indeed bind to a second water molecule this structure is much less frequent, as noted from the Monte Carlo simulation result.

4. Summary and conclusions

The hydrogen bond interaction between acetone and water has been analyzed by ab initio MBPT/CC cluster models using a variety of basis sets. At the highest level the strength of the complex binding is obtained as $5.6 \text{ kcal mol}^{-1}$ with a hydrogen bond distance of $1.961 \text{ \AA}$.

Analysis of the electron correlation effects indicate that in the case of the acetone–water complex the binding energy is insensitive thus suggesting that the dispersion forces are not relevant in this case.

Finally the analysis of the $n \rightarrow \pi^*$ blue shift of acetone in water is made to give a clearer picture of the contribution of the hydrogen bond. Using an optimized geometry for the acetone–water dimer the calculated solvatochromic shift is in excellent agreement with the experimental result. However using the acetone–water (first-neighbor) dimer obtained from the liquid structure of a Monte Carlo simulation this result is considerably lowered. It is suggested that the first hydrogen-bond gives indeed a relatively large contribution to the total shift ($\sim 55\%$) but clearly the cluster calculation using optimized gas phase structure overestimates the hydrogen bond and do not reproduce the situation of the liquid.

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