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Effect of Counterpoise Correction on the Geometries and Vibrational Frequencies of Hydrogen Bonded Systems

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The effect of the counterpoise correction on the geometries and vibrational frequencies of 15 H-bonded systems has been analyzed at the B3LYP and MP2 levels of theory, using the popular 6-31++G(d,p) basis set. The counterpoise correction increases the H-bond distance, decreases the intermolecular stretching frequency and decreases the red-shift of the donor H−X frequency. The observed changes are larger at the MP2 level of theory, for which the basis set superposition error is significantly larger. At both levels of theory, linear relationships between the percentage of BSSE, the relative changes of the H-bond distances and intermolecular stretching frequencies, offer the possibility of estimating, from one single point counterpoise calculation, the geometry and frequencies that one would obtain from a counterpoise corrected potential energy surface.

I. Introduction

The use of finite basis sets in quantum chemical calculations leads to the well-known basis set superposition error (BSSE). This error has been widely recognized, especially for intermolecular H-bonded systems[1−3] and is due to the fact that in the complex, each monomer uses to some extent the basis functions of the other monomer, causing an unphysical energy lowering of the system.

BSSE can be avoided by using sufficiently large basis sets. However, calculations with such basis sets for large systems, like biologically interesting molecules, are impracticable, and so, several approaches have been developed to correct this error,[4−6] the most popular one being the counterpoise (CP) correction of Boys and Bernardi.[4] In most cases, this correction is applied to recalculate the interaction energy of the H-bonded dimer, a posteriori, using the optimized geometries of a potential energy surface not free from BSSE. However, because the unphysical energy lowering of the dimer due to BSSE is not constant in each point of the potential energy surface, decreasing as the distance between the two monomers increases, the normally optimized H-bond distances are too short, and the intermolecular stretching frequencies too large. That is, the shape of the potential energy surface is not the same before or after applying the counterpoise correction.

Several authors have studied the effect of basis set superposition error on the surfaces of several H-bonded systems[7−20] such as $(H_2O)_2$,[8,10−11,14−19] $(HF)_2$,[10,13−14,19] $HF-H_2O$,[7,10,12,19] HF−HCN,[7,9,12] $HCCH-H_2O$,[12] formamide, and formic acid dimers,[14] at different levels of theory. The results show that the intermolecular H-bond distance increases upon optimization with the counterpoise correction, whereas the intermolecular H-bond stretching frequency decreases. The observed changes depend on the level of theory used and are larger if correlation energy is included[12,14,16] at the MP2 level. Moreover, in general, the results show that the weaker the interaction energy is, the larger is the effect of CP on the geometrical parameters, the vibrational frequencies and on the binding energy.[19]

Thus, at first glance, previous results seem to indicate that there is a correlation between the strength of the H-bond and the effect of the counterpoise correction on the geometry and vibrational frequencies of the dimer. If so, it would be interesting to establish such a relation because it would allow us to determine whether reoptimization, including the counterpoise correction, is needed for a particular system or if it is enough to perform single point counterpoise corrections at the normal optimized geometries. In this work, we have studied the effect of counterpoise correction on the potential energy surface of different kinds of hydrogen bonded systems, whose interaction energies range from 1 to 20 kcal/mol. Within this sample, we have included two charged systems, $NH_4^+-H_2O$ and H_2O-HCC^-, as well as two systems with multiple hydrogen bonds: formamidine−formide dimer (FI−FA), which can be taken as model system for the Adenine−Thymine base pair and the formic acid dimer. Our goal in this work is to analyze if such a relation exist or not, for a given basis set at two different levels of calculation: MP2 and B3LYP. The results obtained show that there is not a perfect relation between the strength of the H-bond and the magnitude of the counterpoise correction on the geometries of the dimer. Instead, a much better correlation is obtained between the percentage of BSSE, defined as $(-CP/E_{int})100$, and the relative error of the H-bond distance or the intermolecular stretching frequency.

II. Methods

For all systems, geometry optimizations and vibrational frequencies have been computed using the MP2 method and the nonlocal three-parameter hybrid B3LYP density functional approach.[21,22] MP2 is the most economical post-Hartree−Fock method that accounts for the full range of intermolecular interactions: electrostatic, induction and dispersion effects. In contrast, present DFT approaches do not account for dispersion interactions.[23,24] Despite that, several previous studies[25−35] have shown a reasonably good performance of DFT methods, especially of the popular B3LYP approach, for studying classical or strong H-bonds, for which the electrostatic interactions are dominant. However, for weak H-bonded systems, the dispersion effects become more important, and so, B3LYP is expected to provide too low interaction energies.[35] A comparison of both

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methods will be discussed in the next section. MP2 calculations were performed correlating all the electrons except the 1s-like ones.

BSSE has been corrected using the counterpoise correction of Boys and Bernardi[4]

$$E_{AB}^{CP} = E_{AB}^{\alpha\cup\beta}(AB) + E_{AB}^{\alpha}(A) - E_{AB}^{\alpha\cup\beta}(A) + E_{AB}^{\beta}(B) - E_{AB}^{\alpha\cup\beta}(B) \quad (1)$$

where α and β refer to the basis sets of the A and B fragments, respectively, the parenthesis specify the fragment that is being considered, and the subindex AB is shown to indicate that the taken geometries are those of the supermolecule AB.[11,36] Thus, according to this equation, one needs to calculate five different energies. Counterpoise optimizations can be obtained from the derivatives of eq 1. For a stationary point, first derivatives

$$\frac{\partial E_{AB}^{CP}}{\partial q_j} = \frac{\partial E_{AB}^{\alpha\cup\beta}(AB)}{\partial q_j} + \frac{\partial E_{AB}^{\alpha}(A)}{\partial q_j} - \frac{\partial E_{AB}^{\alpha\cup\beta}(A)}{\partial q_j} + \frac{\partial E_{AB}^{\beta}(B)}{\partial q_j} - \frac{\partial E_{AB}^{\alpha\cup\beta}(B)}{\partial q_j} \quad (2)$$

with respect to all internal coordinates, q_j should be zero. Similarly, the vibrational frequencies can be obtained from second derivatives of eq 1. Simon et al.[12] have implemented such procedure by performing subsequent calls of Gaussian 94[37] program for the dimer and the different monomers with and without ghost functions. The new corrected gradients are used for geometry optimization using the GDIIS method proposed by Császár and Pulay.[38] For charged systems, the CP calculations have been carried out localizing the charge on the corresponding monomer.

All calculations have been performed using the 6-31++G(d,p) basis set. Obviously, the computed counterpoise correction is basis set dependent. We have chosen this basis set for two reasons. First, it is one of the most popular basis sets used in the study of medium and large sized H-bonded systems. Second, Salvador et al.[19] have shown that, especially at the B3LYP level, this basis set provides small BSSE as well as counterpoise corrected values that are in good agreement with those obtained with larger basis sets such as 6-311++G(3df,2pd). Nevertheless, the effect of the basis set will be discussed for one of the studied systems.

III. Results and Discussion

The structures considered for the fifteen H-bonded systems are shown in Figure 1. Frequency calculations confirmed that all structures are minima on the respective potential energy surfaces. The interaction energy, the distance between the two heavy atoms and the intermolecular stretching frequency, obtained with and without applying the counterpoise correction, at the MP2 and B3LYP levels, are given in Tables 1 and 2, respectively. We will first discuss the results obtained at the MP2 level. Next, we will compare the B3LYP results with the MP2 ones.

It can be observed in Table 1 that the interaction energy obtained by adding the CP correction to the normal interaction binding energy (E_{int} + CP) is only slightly less negative than the optimum value computed on the CP corrected potential energy surface (E_{int}^{CP}). This is due to the fact that both the corrected and the uncorrected potential energy surfaces are quite flat near the minimum. Similar results were obtained in previous studies.[11] The larger difference (0.24 kcal/mol) appears for the HCl−H_2S and H_2S−H_2S dimers. In general, the difference is

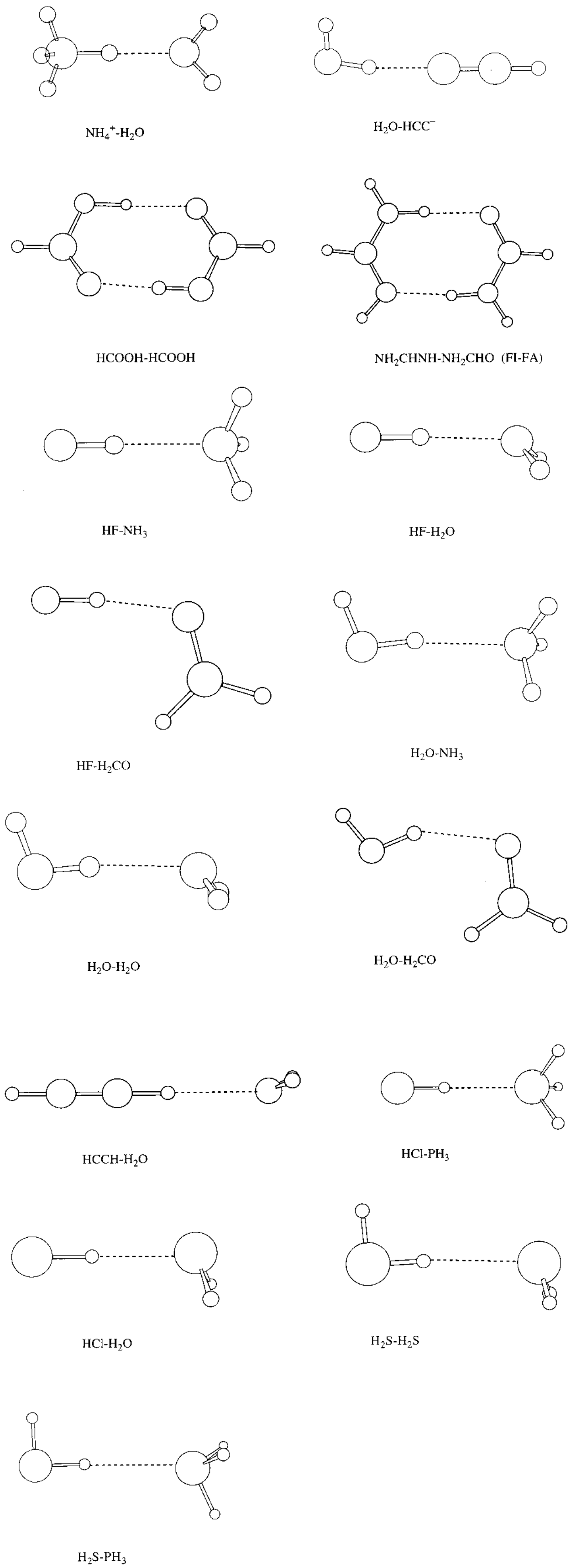

Figure 1. Structures for the fifteen H-bond dimers.

TABLE 1: MP2/6-31++G(d,p) Interaction Energies and CP Correction at the Minimum of the normal Potential Energy Surface (kcal/mol), Interaction Energies in the CP-corrected PES, Distance between Heavy Atoms in the Normal and CP-Corrected PES (Å), Intermolecular Stretching Frequency Corresponding to the Formation of the H-bond (cm^{-1}), and Frequency Shift Corresponding to the X−H Stretching of the Donor Monomer in the Uncorrected and CP-Corrected PES (cm^{-1})

	E_{int}	CP	E_{int} + CP	E_{int}^{CP}	r	r^{CP}	Δr	ν	ν^{CP}	shift	$shift^{CP}$
$NH_4^+-H_2O$	−21.74	1.99	−19.75	−19.79	2.725	2.764	0.039	278	256	419	365
H_2O-HCC^-	−18.52	1.16	−17.36	−17.40	2.876	2.916	0.040	213	197	782	702
$(HCOOH)_2$	−15.58	2.76	−12.82	−12.95	2.721	2.786	0.065	191	176	488	384
FIFA(N−O)	−14.48	2.32	−12.16	−12.21	2.948	3.014	0.066	165	146	348	285
FIFA(N−N)	−14.48	2.32	−12.16	−12.21	2.958	3.025	0.067	165	146	163	128
$HF-NH_3$	−14.37	2.33	−12.04	−12.14	2.637	2.688	0.051	272	238	822	725
$HF-H_2O$	−10.17	1.95	−8.22	−8.30	2.659	2.725	0.066	220	183	384	320
$HF-H_2CO$	−8.47	1.25	−7.22	−7.28	2.671	2.729	0.058	229	201	385	326
H_2O-NH_3	−7.86	1.84	−6.02	−6.14	2.936	3.022	0.086	212	176	209	163
H_2O-H_2O	−6.41	1.65	−4.76	−4.87	2.911	3.008	0.097	203	166	80	65
H_2O-H_2CO	−5.74	1.04	−4.70	−4.76	2.875	2.934	0.059	188	161	83	66
$HCCH-H_2O$	−4.13	1.60	−2.53	−2.68	3.231	3.361	0.130	141	103	41	37
$HCl-PH_3$	−3.93	1.50	−2.43	−2.57	3.865	4.028	0.163	93	65	141	98
$HCl-H_2S$	−3.69	1.50	−2.19	−2.43	3.806	3.983	0.177	94	62	116	86
H_2S-H_2S	−2.10	1.17	−0.93	−1.17	4.141	4.392	0.251	71	35	12	9
H_2S-PH_3	−2.08	1.10	−0.98	−1.10	4.248	4.478	0.230	63	37	19	10

TABLE 2: B3LYP/6-31++G(d,p) Interaction Energies and CP Correction at the Minimum of the normal Potential Energy Surface (kcal/mol), Interaction Energies in the CP-Corrected PES, Distance between Heavy Atoms in the Normal and CP-Corrected PES (Å), Intermolecular Stretching Frequency Corresponding to the Formation of the H-bond (cm^{-1}) and Frequency Shift Corresponding to the X−H Stretching of the Donor Monomer in the Uncorrected and CP-Corrected PES (cm^{-1})[a]

	E_{int}	CP	E_{int} + CP	E_{int}^{CP}	r	r^{CP}	Δr	ν	ν^{CP}	shift	$shift^{CP}$
NH_4+-H_2O	−22.11	0.97	−21.14	−21.15	2.693	2.705	0.012	297	289	592	575
H_2O-HCC^-	−19.41	0.45	−18.96	−18.96	2.837	2.849	0.012	236	230	977	948
$(HCOOH)_2$	−15.80	0.77	−15.03	−15.04	2.668	2.676	0.008	202	199	673	663
FIFA(N−O)	−13.90	0.60	−13.30	−13.31	2.919	2.933	0.014	170	165	457	436
FIFA(N−N)	−13.90	0.60	−13.30	−13.31	2.928	2.945	0.017	170	165	228	217
$HF-NH_3$	−15.26	1.24	−14.02	−14.04	2.615	2.630	0.015	299	287	912	891
$HF-H_2O$	−10.39	1.03	−9.36	−9.38	2.622	2.644	0.022	241	229	471	449
$HF-H_2CO$	−8.64	0.39	−8.25	−8.25	2.636	2.647	0.011	241	235	461	450
H_2O-NH_3	−7.81	1.03	−6.78	−6.82	2.905	2.940	0.035	193	178	278	255
H_2O-H_2O	−6.02	0.85	−5.17	−5.20	2.886	2.933	0.047	204	184	117	108
H_2O-H_2CO	−5.07	0.33	−4.74	−4.75	2.864	2.890	0.026	189	179	105	100
$HCCH-H_2O$	−3.52	0.86	−2.66	−2.71	3.218	3.292	0.074	133	111	60	54
$HCl-PH_3$	−3.65	0.41	−3.24	−3.25	3.781	3.817	0.036	97	89	260	224
$HCl-H_2S$	−3.64	0.43	−3.21	−3.24	3.724	3.759	0.035	99	91	249	217
H_2S-H_2S	−1.46	0.27	−1.19	−1.21	4.175	4.244	0.069	62	53	41	35
H_2S-PH_3	−1.33	0.26	−1.07	−1.08	4.274	4.319	0.045	57	52	39	34

[a] Experimental data: (a) $(HCOOH)_2$, r_{OO} = 2.70 Å [39a]; (b) $HF-NH_3$, r_{FN} = 2.85 Å [39b]; (c) $HF-H_2O$, r_{FO} = 2.66 Å [39c]; (d) $HF-H_2CO$, r_{FO} = 2.87 Å [39d]; (e) H_2O-NH_3, r_{ON} = 3.01 Å [39e]; (f) $(H_2O)_2$, r_{OO} = 2.98 Å [39f,g]; (g) $H_2O-HCCH$, $r_H \cdots O$ = 2.229 Å [39h] MP2/6-31++G(d,p) $r_{H \cdots O}$ = 2.162 Å, $r^{CP}_{H \cdots O}$ = 2.293 Å, B3LYP/6-31G++(d,p) $r_{H \cdots O}$ = 2.145 Å, $r^{CP}_{H \cdots O}$ = 2.220 Å; (h) $HCl-PH_3$, r_{ClP} = 3.88 Å [39i]; and (i) $HCl-H_2S$, r_{ClS} = 3.809 Å [39j].

only about 0.1 kcal/mol or less, regardless of whether we take the normal geometry or the counterpoise corrected one.

It can be observed in Table 1 that, as expected, the counterpoise correction increases the H-bond distance. Consequently, the intermolecular stretching frequency decreases and so, the red-shift of the donor H−X frequency becomes smaller. As a general trend, it is observed that the larger the H-bond interaction is, the smaller is the change on the H-bond distance. However, there are some exceptions. For example, the binding energy of $HF-H_2O$ is greater than that of $HF-H_2CO$, whereas the change on the O−F bond distance by applying the counterpoise correction is larger for $HF-H_2O$. Also, the geometrical change in H_2S-PH_3 is smaller than in H_2S-H_2S, even though the binding energies of the two systems are very similar, the one of H_2S-PH_3 being slightly smaller. Given that, in general, the observed geometrical changes are smaller for the stronger H-bonded systems, one would initially expect that the stronger interacting systems would show smaller changes on the intermolecular stretching frequencies. However, such a trend is not observed, neither for the intermolecular stretching frequency nor for the change in the H−X frequency red-shift. On the other hand, it can be observed in Table 1 that there is not any correlation between the magnitude of CP and the changes on the geometries and vibrational frequencies of these systems.

However, the analysis of the results has shown that there is a very good correlation between the percentage of the BSSE, $(-CP/E_{int})100$, and the relative change on the H-bond distance $(\Delta r/r)100$, as well as between the percentage of the BSSE and the relative change of the intermolecular stretching frequency $(\Delta\nu/\nu)100$. Figures 2 and 3 show these relationships. As expected, the larger the percentage of BSSE is, the larger is the relative change of the distance between the two heavy atoms or the change of the intermolecular stretching frequency. For the weaker interacting systems, H_2S-H_2S and H_2S-PH_3, for which the percentage of BSSE is about 50%, the geometrical changes can be as large as 0.25 Å. For classical H-bond systems, such as H_2O-H_2O, with a 25% of BSSE, the geometrical change (∼0.1 Å) is also significant. The existence of such correlations is important because it allows us to estimate, from the normal interaction energy and one single counterpoise calculation, the

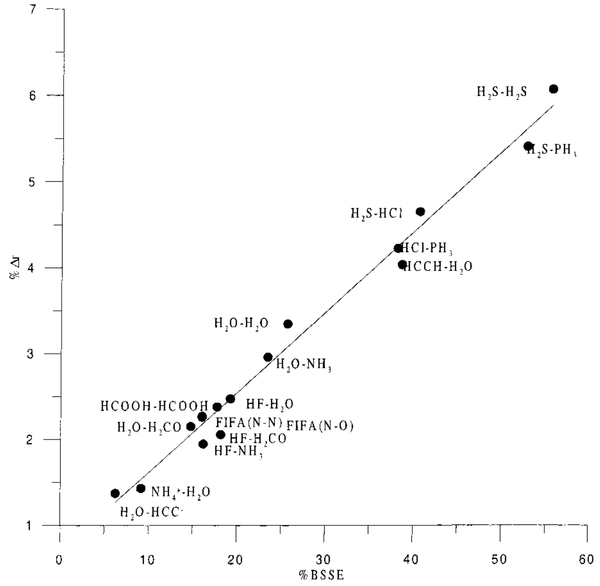

Figure 2. Percentage of BSSE ($-CP/E_{int}$)100 versus relative change on the H-bond distance ($\Delta r/r$)100 computed at MP2/6-31++G(d,p) level. % $\Delta r = 0.093\%$ BSSE + 0.676; $r^2 = 0.98$.

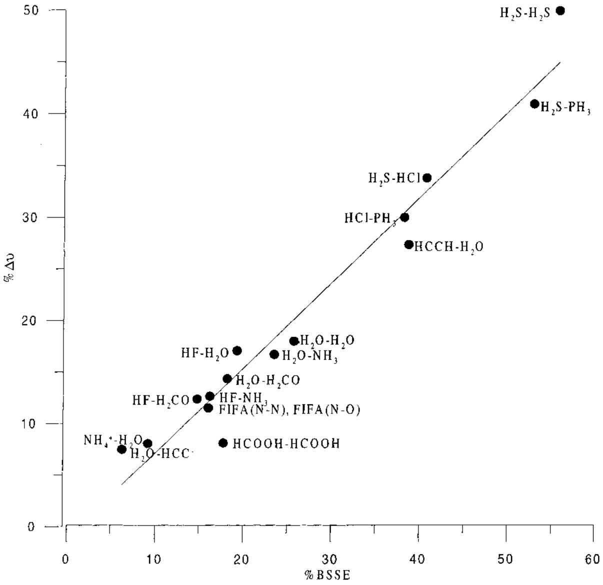

Figure 3. Percentage of BSSE ($-CP/E_{int}$)100 versus relative change on the H-bond intermolecular stretching frequency ($\Delta\nu/\nu$)100 computed at MP2/6-31++G(d,p) level. % $\Delta\nu = 0.828\%$ BSSE + 0.96; $r^2 = 0.96$.

magnitude of the error introduced on the H-bond distances and on the intermolecular vibrational frequencies due to basis sets limitations.

As it was to be expected, at the B3LYP level, the counterpoise correction also increases the H-bond distance, and decreases the intermolecular stretching frequency and the red-shift of the H−X frequency. Also, the corrected interaction energies at the standard optimized geometries (E_{int} + CP) are almost the same than those obtained from the counterpoise corrected potential energy surfaces (E_{int}^{CP}). At this level of theory, the differences between E_{int} + CP and E_{int}^{CP} are even smaller than at the MP2 level.

A comparison of Tables 1 and 2 shows, however, several differences between the two levels of calculation. First, it is observed that the uncorrected interaction energies of the stronger systems, with the exception of the formamidine−formamide dimer, are more negative at the B3LYP level than at the MP2 one, even though the dispersion energy is not covered by present density functional approaches.[23,24] The largest differences are observed for the H_2O-HCC^- and $HF-NH_3$ dimers for which the B3LYP interaction energies are 0.89 kcal/mol more negative than the MP2 ones. This confirms that the dominant term in the stronger interacting systems is electrostatic, the dispersion effects being a minor component of the total interaction energy. In contrast, the uncorrected interaction energies of the weaker H-bond systems are less negative at the B3LYP level. Because the counterpoise correction is larger at the MP2 level than at the B3LYP one, the B3LYP and MP2 CP corrected interaction energies show larger differences for the stronger systems, whereas they become closer for the weaker ones.

With respect to the geometry changes, it can be observed that, except for the two weakest systems, H_2S-H_2S and H_2S-PH_3, the optimized H-bond distance in the uncorrected potential energy surface, is always smaller at the B3LYP level. For most systems, the differences between the B3LYP and MP2 results range from 0.01 to 0.04 Å. There are two dimers, $HCl-H_2S$ and $HCl-PH_3$, that show larger differences (0.08 Å). As expected, the effect of the CP correction on the H-bond distance (Δr) is larger at the MP2 level of calculation, given that the CP is larger at this level of theory. Thus, the differences between the MP2 and B3LYP computed H-bond distances increase after applying the counterpoise correction.

The computed uncorrected intermolecular stretching frequencies are, in general, larger at the B3LYP level. This is in agreement with the fact that the H-bond distances are computed to be smaller at this level of theory. As for the H-bond distances, the effect of the counterpoise correction on the intermolecular stretching frequencies is smaller with the B3LYP method. At this level, the decrease ranges from 3 to 22 cm^{-1}, whereas at the MP2 one the differences go from 15 to 38 cm^{-1}. Consistently with these findings, the frequency shift corresponding to the X−H of the donor monomer is always larger at the B3LYP level, the differences increasing after including the counterpoise correction.

Despite these differences, and similarly to MP2, the analysis of the results shows that the best correlations found are those between the percentage of the BSSE ($-CP/E_{int}$)100 and the relative change on the H-bond distance ($\Delta r/r$)100, or between the percentage of the BSSE and the relative change of the intermolecular stretching frequency ($\Delta\nu/\nu$)100. Figures 4 and 5 show these correlations. At the B3LYP level of theory, however, these relationships are not as good as those found at the MP2 level. Note that the obtained correlation coeficient r^2 in the ($-CP/E_{int}$)100 versus ($\Delta r/r$)100 plot is 0.82 compared to the 0.98 value determined at the MP2 level. However, if the results of the weakest H_2S-PH_3 dimer are not included, the correlation improves significantly, the r^2 value being now 0.92. Similarly, the correlation between the percentage of BSSE and the relative change of the intermolecular stretching frequency improves significantly (from 0.87 to 0.94) if the results of H_2S-PH_3 are not considered.

Let us now compare with the known experimental data,[39] which are included in Table 2. It should be mentioned that the intermolecular H-bonding vibrations are anharmonic, and so, the experimental distances are expected to be somewhat longer than those obtained from the minimum of the potential energy surface. For all the known systems, the computed B3LYP H-bond distances are too small compared to the experimental values. The CP correction increases the distances in such a way that they become closer to the experimental ones. Except for the $HF-NH_3$ and $HF-H_2CO$ systems, for which the computed

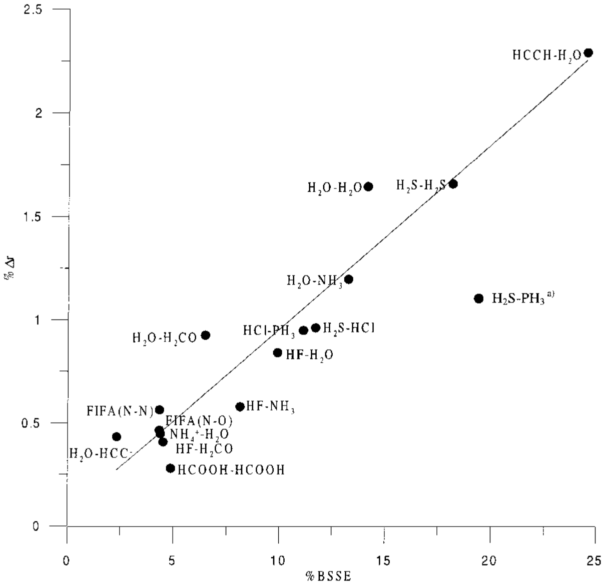

Figure 4. Percentage of BSSE ($-CP/E_{int}$)100 versus relative change on the H-bond distance ($\Delta r/r$)100 computed at B3LYP/6-31++G(d,p) level. % $\Delta r = 0.089\%$ BSSE + 0.062; $r^2 = 0.92$. (If H_2S-PH_3 is included in the regression the new equation will be % $\Delta r = 0.078\%$ BSSE + 0.126; $r^2 = 0.82$)

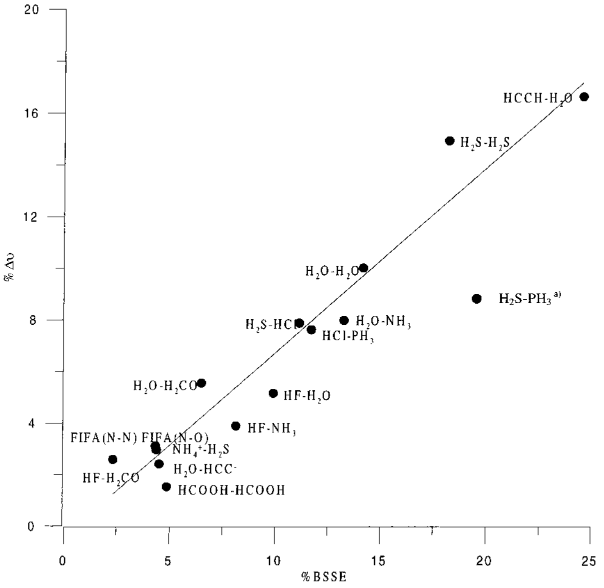

Figure 5. Percentage of BSSE ($-CP/E_{int}$)100 versus relative change on the H-bond intermolecular streching frequency ($\Delta\nu/\nu$)100 computed at B3LYP/6-31++G(d,p) level. % $\Delta\nu = 0.718\%$ BSSE − 0.446; $r^2 = 0.94$. (If H_2S-PH_3 is included in the regression the new equation will be % $\Delta\nu = 0.645\%$ BSSE − 0.021; $r^2 = 0.87$)

distances are 0.22 Å too small, the differences range from 0.02 to 0.07 Å. However, at the MP2 level, also with the exception of the $HF-NH_3$ and $HF-H_2CO$ dimers, the increase due to the CP correction leads to optimized distances that are too large, the uncorrected values being in many cases in better agreement with the experimental results than the CP optimized ones. Thus, the present results seem to indicate that the effect of the CP correction on the geometry is too large at this level of theory.

Several dimers, especially the H_2O-H_2O one, have been extensively studied theoretically using larger basis sets.[40-43] In particular, calculations with the 6-311++(3df,2pd) basis set provide an intermolecular O−O distance of 2.919(2.911 Å) at the B3LYP(MP2) levels, respectively, which after applying the counterpoise correction increase to 2.931(2.950 Å).[19] Thus, as expected, the effect of the counterpoise correction on the H-bond distance is smaller with the larger basis set because the BSSE is smaller. The comparison of these results with the ones obtained in the present work with the 6-31++G(d,p) basis set indicates that at the B3LYP level the CP optimized distance (2.933 Å) is very similar to that obtained with the larger basis set. At the MP2 level, however, the CP corrected distance with the smaller basis set (3.008 Å) is significantly larger than the one obtained with the larger basis. Similar observations are found for the $HF-H_2O$ dimer.[19] Thus, B3LYP method appears to converge more rapidly than the MP2 one.

In summary, the present study has shown that there is a quite good correlation between the percentage of BSSE and the relative change of the H-bond distance or the relative change of the intermolecular stretching frequency. These correlations allows us to get, from one single point counterpoise calculation, a first estimation of the magnitude of the effect of the counterpoise correction on the geometry and vibrational frequencies of a H-bonded system at two different, very commonly used, levels of theory. Obviously, different basis sets and different theoretical methods will provide other relationships. However, results for the $(H_2O)_2$ dimer with other basis sets, such us the 6-311++G(d,p), 6-311++G(2df,2p) and 6-311++G-(3df,2pd) ones, at the MP2 level, indicate that the obtained correlation still holds for these other basis. In any case, it would be interesting to analyze if the good correlations found in the present work still remain for other systems, other methods or other basis sets.

IV. Conclusions

The effect of the counterpoise correction on the geometries and vibrational frequencies of fifteen H-bonded systems has been analyzed at the B3LYP and MP2 levels of theory, using the popular 6-31++G(d,p) basis set.

The counterpoise correction increases the H-bond distance, decreases the intermolecular stretching frequency and decreases the red-shift of the donor H−X frequency. The observed changes are larger at the MP2 level of theory, given that the computed BSSE is significantly larger at this level of theory.

For both methods, especially for the MP2 one, a nice correlation has been found between the percentage of BSSE ($-CP/E_{int}$)100 and the relative change of the intermolecular H-bond distance, or between the percentage of BSSE and the relative change of the intermolecular stretching frequency. For the stronger interacting systems, which in general present smaller % BSSE, the geometry changes produced by the counterpoise correction are quite small, whereas for the weaker systems, the geometry changes, at the MP2 level, can be as large as 0.25 Å. The linear relationships obtained allows us to estimate, from one single counterpoise calculation on the normal potential energy surface, the H-bond distance and the intermolecular stretching frequency that one would obtain if optimizations were performed on a CP corrected potential energy surface. An extension of these relationships to other kind of H-bonded systems is being in progress in our laboratory.

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