
BSSE-Corrected Geometry and Harmonic and Anharmonic Vibrational Frequencies of Formamide–Water and Formamide–Formamide Dimers

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Received 8 November 2004; accepted 17 December 2004

Published online 22 March 2005 in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/qua.20536

ABSTRACT: The basis set superposition error (BSSE) influence in the geometry structure, interaction energies, and intermolecular harmonic and anharmonic vibrational frequencies of cyclic formamide–formamide and formamide–water dimers have been studied using different basis sets (6-31G, 6-31G**, 6-31++G**, D95V, D95V**, and D95V++**). The a posteriori “counterpoise” (CP) correction scheme has been compared with the a priori “chemical Hamiltonian approach” (CHA) both at the Hartree–Fock (HF) and second-order Møller–Plesset many-body perturbation (MP2) levels of theory. The effect of BSSE on geometrical parameters, interaction energies, and intermolecular harmonic vibrational frequencies are discussed and compared with the existing experimental data. As expected, the BSSE-free CP and CHA interaction energies usually show less deep minima than those obtained from the uncorrected methods at both the HF and MP2 levels. Focusing on the correlated level, the amount of BSSE in the intermolecular interaction energies is much larger than that at the HF level, and this effect is also conserved in the values of the force constants and harmonic vibrational frequencies. All these results clearly indicate the importance of the proper BSSE-free correlation treatment with the well-defined basis functions. At the same time, the results show a good agreement between the a priori CHA and a posteriori CP correction scheme; this agreement is remarkable in the case of large and well-balanced basis sets. The anharmonic frequency correction values also show an important BSSE dependence, especially for hydrogen bond stretching and for low frequencies belonging to the intermolecular normal modes. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 103: 841–853, 2005

Key words: BSSE; CHA; formamide dimer; formamide–water; anharmonic frequency

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1. Introduction

The study of van der Waals interactions and hydrogen bonds is important to understand the structure of biologically important macromolecules, such as proteins and polynucleic acids. Formamide (FA) is the simplest molecule that contains a peptide linkage built by the carbonyl and amino groups; therefore, we can consider the formamide dimer (FA–FA) as the simplest model of the pairing of nucleic acids and the formamide–water (FA–WA) complex as a hydration of proteins, respectively. Geometry structures [1–10] and vibrational spectra [2, 6, 11–14] of the FA–FA and FA–WA dimers have been the subject of many studies using different *ab initio* [Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory (MP2)] methods, which give valuable information about the structure and dynamics of the H-bonds in molecular systems.

It has been recognized that basis set supposition error (BSSE) [15] represents an unbalanced effect between the energies of complex and its fragments in the computation of interaction energy [16–18]. This phenomenon is related to the LCAO approximation that affects the whole description of the complex, i.e., stationary points [19–21], vibration harmonic [20–22] and anharmonic frequencies, wave function [23], etc. The BSSE is a pure “mathematical effect” and it is an important problem to solve when we study a weakly bonded molecular complex. This effect appears only as a result of the use of finite basis sets, because the description of the monomer is actually better within the supermolecule than that which one has for the free monomers by applying the same basis set, so thus leads to incomplete description in the individual monomers. Due to BSSE, the calculated interaction energies show too deep minima, and the computed potential energy surface (PES) is distorted.

The most important and straightforward a posteriori correction scheme, the so-called “function counterpoise” (CP), or simply the Boys–Bernardi method, was introduced by Jansen and Ross [15] and, independently, by Boys and Bernardi [24] in 1969/1970. In this CP scheme, the monomer energies are recalculated by using the whole supermolecular basis set and these corrected monomers are used in the molecular interaction energy calculations. A conceptually different way to handle the BSSE problem is to apply the “chemical Hamiltonian approach” (CHA) for the case of intermolecu-

lar complexes proposed by Mayer [25] in 1983. (For a detailed review on CHA, see Ref. [26].) By using the a priori CHA method one can eliminate the nonphysical terms of the Hamiltonian, which leads to wave functions free from the nonphysical delocalizations caused by BSSE. Using this CHA scheme, several approaches have been developed both at the HF [27–37] and correlated [38–45] levels of theory to study the structures and interaction energies for different van der Waals and hydrogen-bonded systems.

In our previous works [17, 18] we have shown that the BSSE content of the FA–FA binding energy is strongly dependent on the basis sets applied; the magnitude of this content is very significant. As a consequence, it can be ascertained that the first, second, and higher derivatives of energy in accord with the internal coordinate also contain BSSE effects.

In the present article we investigate the geometry structures, binding energies, and harmonic vibrational frequencies of the FA–FA and FA–WA applying both the CP and CHA methods. The BSSE effects in the anharmonic frequencies are studied, using the CP method.

The methods employed (CP, CHA/CE, and CHA/MP2) are briefly explained in the next section. In Section 3 the results for FA–FA and FA–WA are presented in different basis sets (6-31G, 6-31G**, 6-31++G**, D95V, D95V**, and D95V++**) and the obtained geometry structures, binding energies, and harmonic and anharmonic vibrational frequencies are compared and discussed. Our conclusions are given in the final section.

2. The Methods Applied (CP, CHA/CE, and CHA/MP2)

2.1. THE CP SCHEME

The simplest definition of the uncorrected interaction energy between two molecules is the difference of the supermolecular energy and the sum of the free monomer energies, each calculated in its own basis set:

$$\Delta E_{AB}^{\text{unc}} = E_{AB}(AB) - E_A(A) - E_B(B), \quad (1)$$

where $E_{AB}(AB)$, $E_A(A)$, and $E_B(B)$ denote the total energy of the AB “supermolecule” and the energy of the A and B monomers, respectively. The notations in parentheses indicate that basis sets corre-

sponding to (sub)system A , B , and AB , respectively, were used. To compute the correct value of the interaction energy $\Delta E_{AB}^{\text{unc}}$, we need to use (nearly) complete basis sets on the supermolecule and on each monomer, which is usually impossible in practice.

In the CP scheme, the interaction energy $\Delta E_{AB}^{\text{CP}}$ is defined as the difference of the supermolecule and monomer energies, all computed in the same supermolecule basis set:

$$\Delta E_{AB}^{\text{CP}} = E_{AB}(AB) - E_A(AB) - E_B(AB). \quad (2)$$

Using Eqs. (1) and (2), one can define the BSSE content in the interaction energy as

$$\delta E_{\text{BSSE}} = \Delta E_{AB}^{\text{unc}} - \Delta E_{AB}^{\text{CP}} = E_A(AB) - E_A(A) + E_B(AB) - E_B(B). \quad (3)$$

According to Eq. (3), the CP-corrected potential energy surface (PES) of the dimer becomes

$$E^{\text{CP}}(AB) = E_{AB}^{\text{unc}}(AB) - \delta E_{\text{BSSE}} = E_{AB}^{\text{unc}}(AB) - E_A(AB) + E_A(A) - E_B(AB) + E_B(B). \quad (4)$$

Equation (4) shows that by considering only the intermolecular internal coordinates as optimized parameters one has to calculate three different total energies to determine the CP-corrected PES.

2.2. THE CHA SCHEME

In the alternative a priori CHA scheme introduced by Mayer [25, 26] one can omit the BSSE-caused terms of the Hamiltonian, which is a conceptually different way of handling the BSSE problem. The CHA procedure permits the supermolecule calculations to remain consistent with those for the free monomer performed in their original basis sets. The basic idea of Mayer's scheme is that one can divide the Born–Oppenheimer Hamiltonian into two parts:

$$\hat{H}_{\text{BO}} = \hat{H}_{\text{CHA}} + \hat{H}_{\text{BSSE}}, \quad (5)$$

where \hat{H}_{CHA} is the BSSE-free part of the Hamiltonian and \hat{H}_{BSSE} is the “unphysical” part of the Hamiltonian that is responsible for the BSSE. The only difficulty of this scheme is that the resulting “physical” Hamiltonian \hat{H}_{CHA} is not Hermitian, so one cannot expect the BSSE-free Hamiltonian \hat{H}_{CHA} to

be Hermitian either. Based on this CHA Hamiltonian, Mayer and Vibók developed different SCF-type equations [28]:

$$\hat{H}_{\text{CHA}}\Psi_{\text{CHA}} = \Lambda\Psi_{\text{CHA}}, \quad (6)$$

$$E_{\text{CHA/CE}} = \frac{\langle\Psi_{\text{CHA}}|\hat{H}_{\text{BO}}|\Psi_{\text{CHA}}\rangle}{\langle\Psi_{\text{CHA}}|\Psi_{\text{CHA}}\rangle}. \quad (7)$$

In the CHA framework [32–35] described by Eqs. (6)–(7) the non-Hermitian CHA Hamiltonian \hat{H}_{CHA} is used only to provide the BSSE-free wave function (or a perturbative approximation to it) but the energy should be calculated by using the conventional (Hermitian) Born–Oppenheimer Hamiltonian \hat{H}_{BO} , making not trivial the question of how one should calculate the second-order energy correction.

The zeroth-order Hamiltonian is defined in terms of the CHA Fockian [45]:

$$\hat{H}^0 = \sum_p \varepsilon_p \hat{\phi}_p^+ \hat{\phi}_p^-, \quad (8)$$

where $\hat{\phi}_p^+$ and $\hat{\phi}_p^-$ are the creation and annihilation operators.

To obtain the first-order wave function in the perturbation theory, the non-Hermitian CHA Hamiltonian could be partitioned as

$$\hat{H}_{\text{CHA}} = \hat{H}^0 + \hat{V}_{\text{CHA}}, \quad (9)$$

where \hat{H}^0 , defined by Eq. (8), is the Møller–Plesset-type unperturbed Hamiltonian, which is also non-Hermitian, and \hat{V}_{CHA} represents the perturbation. At the same time, the perturbation energy could be obtained considering the following partition of the Born–Oppenheimer Hamiltonian \hat{H}_{BO} :

$$\hat{H}_{\text{BO}} = \hat{H}^0 + \hat{V}. \quad (10)$$

Then the energy up to second order could be presented as

$$E^{(2)} = \frac{\langle\Psi_0|\hat{H}_{\text{BO}}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + J_2, \quad (11)$$

where J_2 is the generalized Hylleraas functional:

$$J_2 = \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} [2 \operatorname{Re}(\langle \hat{Q} \Psi_1 | \hat{V} | \Psi_0 \rangle) + \operatorname{Re}(\langle \Psi_1 | \hat{H}^0 - E_0 | \Psi_1 \rangle)]. \quad (12)$$

Here Ψ_0 is the unperturbed wave function, E_0 is the zero order energy ($\hat{H}^0 \Psi_0 = E_0 \Psi_0$), Ψ_1 is the first-order wave function of the perturbation, and \hat{Q} is the projection operator on to the orthogonal complement to Ψ_0 . These equations define our working formula at the second-order perturbation level. This formalism is called "CHA/MP2" theory [40].

3. Computational Details

The calculations were carried out in Heidelberg on a Hewlett-Packard cluster. The standard HF, MP2, and CP-corrected HF/MP2 calculations were performed using the Gaussian 03 computer code [46]. The CHA/CE- and CHA/MP2-type calculations were done by generating the input data (integrals and RHF orbitals) with a slightly modified version of HONDO-8 [47]. In these calculations the CHA/SCF code [28] and the CHA/MP2 program of Mayer and Valiron [40, 42] were used. For the frequency calculations based on Wilson's G-F method, the program written by Beu [48] was applied.

We considered six different basis sets: 6-31G, 6-31G**, 6-31G**+, D95V, D95V**, and D95V+**. 6-31G to 6-31G**+ are standard Pople basis sets; D95V to D95V+** are Dunning/Huzinaga valence basis sets.

The conventional supermolecule geometries were optimized at both the HF and MP2 levels, applying the analytical gradient method included in the Gaussian 03; the CHA- and CP-corrected geometries were calculated by using a numerical gradient method [inverse parabolic interpolation (IPI) [49]] in internal coordinates including only internal coordinates with intermolecular character (one bond, two angles, and three torsion angles). The reason for this choice is that the CPU time of MP2-CHA program is fairly big. To test the applicability of our numerical gradient method we performed several sample calculations using both the IPI method and the analytical gradient built into Gaussian 03. There is practically no difference between them. For conventional uncorrected cases we also performed similar calculations to check the values of the force constants and harmonic vibrational frequencies. The uncorrected HF and MP2

results for the force constants (in internal coordinates) and for the harmonic vibrational frequencies were obtained by using the standard routines of the Gaussian 03 program. As for the CHA- and CP-corrected calculations, at first the numerical second derivatives of the energies were calculated to obtain the CHA and CP force constants and then the NOMAD program [48] was applied to obtain the appropriate CHA and CP harmonic vibrational frequencies. As we are interested in the BSSE content in the molecular interaction energies, only those components of the force constant matrix were recalculated that correspond to intermolecular internal coordinates. The anharmonic frequencies were obtained using the standard full-CP method implemented in Gaussian 03.

4. Results and Discussion

In this section we report and discuss the results obtained for the FA-FA and FA-WA complexes. The geometry structures and the energetic properties are dealt for the FA-FA and FA-WA dimers, followed by the intermolecular harmonic and anharmonic frequency results obtained for the same systems.

4.1. INTERACTION ENERGY AND GEOMETRY STRUCTURE

Formamide-Formamide Dimer

Table I shows the optimized geometry parameters for the FA-FA complex (Fig. 1), using the conventional (Uncorr.), CHA, and CP schemes at both the HF and MP2 levels. The FA-FA dimer has planar geometry configuration: the global minimum for the dimer is a cyclic structure of C_{2h} symmetry involving two equivalent $N-H \cdots O=C$ intermolecular hydrogen bonds. Two other planar minima has been identified [2, 8, 18] that establish a single $N-H \cdots O=C$ hydrogen bond building up the linear and zig-zag configurations. In the present article we consider just the planar cyclic dimer configuration, for which the BSSE-corrected geometrical parameters are presented. Once this assumption is made, the only variables left are the r_{HO} bond length and two angles, α_{NHO} and α_{HOC} , that could be associated with the in-plane vibration normal modes, while all three torsion angles having intermolecular character are kept constants, their normal modes representing out-of-plane vibrations.

TABLE I

Intermolecular coordinate for the FA-FA dimer computed at the HF and second-order Møller-Plesset perturbation theory (Uncorr., CHA, CP) level, using D95V, D95V**, D95V+**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	Method	r_{HO} (Å) ^a		α_{NHO}^1 (Deg.)		α_{HOC}^2 (Deg.)	
		RHF	MP2	RHF	MP2	RHF	MP2
D95V (66)	Uncorr.	1.904732	1.872102	129.695	125.899	165.563	169.283
	CHA	1.949505	1.935613	128.922	125.125	166.332	170.077
	CP	1.943000	1.960082	129.418	125.691	165.842	169.494
D95V** (120)	Uncorr.	2.001795	1.862177	125.687	122.053	168.902	172.599
	CHA	2.029317	1.911865	125.028	122.097	169.551	172.582
	CP	2.019053	1.924170	124.931	121.827	169.678	172.830
D95V+** (150)	Uncorr.	2.020500	1.873623	125.242	120.921	169.385	173.680
	CHA	2.038619	1.951182	125.209	122.475	169.433	172.144
	CP	2.033882	1.936152	125.235	122.369	169.379	172.249
6-31G (66)	Uncorr.	1.919157	1.912499	126.848	121.962	168.019	172.365
	CHA	1.934196	1.922721	126.818	123.044	168.036	171.298
	CP	1.938718	1.965316	127.580	123.663	167.282	170.666
6-31G** (120)	Uncorr.	1.998099	1.886595	122.711	118.959	171.454	174.968
	CHA	2.007080	1.898483	123.644	120.909	170.526	173.035
	CP	2.025159	1.946695	123.617	120.374	170.557	173.563
6-31++G** (150)	Uncorr.	2.016919	1.898734	125.409	121.739	169.152	172.796
	CHA	2.033988	1.954470	125.127	122.642	169.428	171.905
	CP	2.037998	1.953893	125.216	122.483	169.341	172.065

The number of basis functions are given in parentheses.

^a Experimental value ≈ 1.9 Å, taken from Ref. [9].

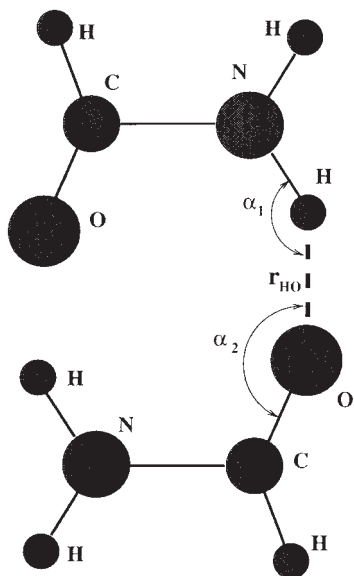


FIGURE 1. Formamide-formamide dimer.

The results show that only the r_{HO} bond length has an important BSSE correction (0.06 Å for MP2-CHA/6-31++G**, 0.08 Å for MP2-CHA/D95V+**, and 0.06 Å for MP2-CP/6-31++G** and MP2-CP/D95V+**), which increases the bond size.

Furthermore the change in the α_{NHO} and α_{HOC} angle values is insignificant but their corresponding force constants also include BSSE effects. Unfortunately, the experimental value for r_{HO} bond length presented in Ref. [9] does not have the desired precision, so we could not compare with high precision the uncorrected values and the given BSSE-corrected bond lengths. Both the corrected and the uncorrected values are close to the experimental value, ≈ 1.9 Å (1.87 Å for MP2/D95V+** and 1.9 Å for MP2/6-31++G** in the uncorrected case; 1.95 Å for the CHA- and CP-corrected cases). However, we can compare our calculated result for the r_{NO} intermolecular distance with the experimental values obtained by Itoh and Shimanouchi [12]. The calculated lengths are 2.895 Å for the uncorrected case, 2.970 Å for CHA-type, and 2.955 Å for CP-type BSSE-corrected cases, while the X-ray data for the formamide crystal [12] gives 2.935 Å for the r_{NO}

TABLE II

Interaction energies^a (in kcal/mol) for different FA-FA dimer geometry computed at the HF and second-order Møller-Plesset perturbation theory (Uncorr., CHA, CP) level, using D95V, D95V**, D95V+**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	D95V		D95V**		D95V+**		6-31G		6-31G**		6-31++G**	
	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2
Uncorr.	-17.018	-18.370	-12.912	-16.921	-12.043	-15.903	-17.387	-18.799	-14.212	-18.330	-12.385	-15.365
CHA	-15.279	-14.511	-12.086	-13.971	-11.567	-13.140	-15.580	-14.496	-12.576	-13.851	-11.965	-13.228
CP	-15.185	-14.046	-11.886	-13.552	-11.547	-13.201	-14.956	-13.705	-12.032	-13.492	-11.837	-13.399

^a Experimental value ≈ -13.967 kcal/mol; taken from Ref. [9].

intermolecular distance. If we suppose that the intermolecular bond length in the crystal phase is a bit shorter than in the gas phase, it can be considered that the corrected values are very close to the experimental.

In Table II we present the calculated intermolecular binding energies, considering the optimized geometry in the given basis and using the given methods (uncorrected, CHA, and CP) and levels of theory (RHF and MP2). The experimental value was obtained using Rydberg electron transfer technique between laser-excited atoms; the molecular systems [9] is 606 meV, which corresponds to 13.967 kcal/mol. Our BSSE-corrected results (13.288 kcal/mol for MP2-CHA/6-31++G**, 13.399 kcal/mol for MP2-CP/6-31++G**, 13.140 kcal/mol for MP2-CHA/D95V+**, and 13.201 for MP2-CP/D95V+**) are very close to experimental values, whereas the uncorrected results show more than 1.4 kcal/mol difference. Moreover, we can obtain reasonable binding energy value even if we use the 6-31G and D95V bases without diffuse or polarization functions, applying BSSE correction for uncorrected geometry at the same time.

Formamide-Water Dimer

The optimized geometry parameters for the FA-WA complex (Fig. 2), considering the conventional (Uncorr.), CHA, and CP cases both at the HF and MP2 levels, are given in Table III. The FA-WA molecular system has a nearly planar geometry configuration, and all the torsion angles are close to 0° or 180° value except one. This exception corresponds to the τ_{NHOH} torsion angle, where the “nonbonded” hydrogen atom of the water molecule that belongs to the τ_{NHOH} torsion coordinate rises from the plane of the “molecular complex.” In this case we considered, as an optimization parameter, all the internal coordi-

nates of applied Z-matrix with intermolecular character; but in Table IV we present only those four parameters (r_{HO} , α_{NHO} , α_{HOH} , and τ_{NHOH}). The results show that only the r_{HO} bond length and τ_{NHOH} torsion angle have an important BSSE correction; the change in the α_{NHO} and α_{HOH} angles is insignificant but their force constants also contain BSSE effects. In case of the r_{HO} bond length the BSSE corrections (bond length increase) at the MP2 level are about 0.07 Å but at the HF level this bond extension is only 0.02 Å. These BSSE correction effects are similar to the FA-FA molecular complex. Similar to the r_{HO} bond the τ_{NHOH} torsion angle also shows an important BSSE content, which is quite basis dependent. Application of diffuse and polarization functions is important to obtain the required description. Using such basis sets it can be observed that the BSSE corrections try to come the nonbonded hydrogen of the water molecule near to the planar geometry configuration. In the experimen-

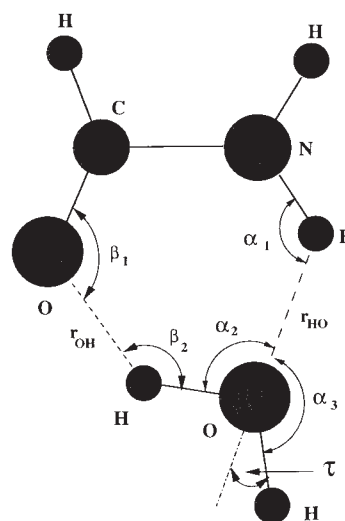


FIGURE 2. Formamide-water dimer.

TABLE III

Intermolecular coordinate for the FA-FA dimer computed at the HF and second-order Møller-Plesset perturbation theory (Uncorr., CHA, CP) levels, using D95V, D95V**, D95V++**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	Method	r_{HO} (Å)		α_{NHO}^1 (Deg.)		α_{HOH}^2 (Deg.)		τ_{NHOH} (Deg.)	
		RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2
D95V (46)	Uncorr.	2.057421	1.965266	137.178	137.931	87.167	89.066	180.000	180.000
	CHA	2.064056	1.983627	138.154	138.707	87.308	89.720	180.000	180.000
	CP	2.069251	2.013312	137.775	139.099	87.054	88.174	180.000	180.000
D95V** (85)	Uncorr.	2.197833	2.033782	138.472	138.888	80.333	80.997	138.124	127.815
	CHA	2.196117	2.060630	139.052	139.320	81.405	83.227	148.176	140.709
	CP	2.199887	2.078997	138.690	139.870	81.072	81.804	152.538	144.343
D95V++** (106)	Uncorr.	2.217492	2.049920	137.800	138.175	81.277	82.198	149.293	138.013
	CHA	2.234205	2.114888	138.005	139.672	81.586	84.119	162.284	146.050
	CP	2.236823	2.125583	137.480	138.804	81.073	81.778	162.675	149.179
6-31G (46)	Uncorr.	2.018338	1.978192	138.242	139.650	86.328	84.985	180.000	143.246
	CHA	2.017132	1.958153	138.525	139.281	87.467	89.287	180.000	177.117
	CP	2.020008	1.976003	138.703	140.481	86.932	87.649	180.000	178.941
6-31G** (85)	Uncorr.	2.158679	2.016780	139.681	140.679	79.124	79.414	121.962	113.069
	CHA	2.152501	2.035380	139.543	140.436	81.979	83.712	142.339	135.197
	CP	2.172080	2.066211	139.955	141.918	80.209	80.291	142.009	131.754
6-31++G** (106)	Uncorr.	2.198398	2.052351	137.664	137.848	81.846	82.991	155.426	142.656
	CHA	2.218969	2.121234	137.947	139.095	81.749	84.417	164.663	149.774
	CP	2.223408	2.121777	137.809	138.270	81.236	82.094	163.248	152.353

The number of basis functions are given in parentheses.

tal case this value is about 15° [13], whereas the BSSE-corrected value (MP2-CHA/D95V**++) gives $\approx 32^\circ$. Because this experimental value was obtained using the fit of out-of-plane movement of the proton by rotation about the OH bond involved in the hydrogen bond, keeping all the other hydrogen atoms in molecular plane, we consider that this value is slightly underestimated because the rest of the hydrogen atoms are also out of the molecular plane formed by the heavy atoms. On the other hand, using high-polarization functions in applied basis sets the calculated results for τ_{NHOH} torsion angle will remain closer to the experimental value.

TABLE IV

Calculated (MP2-CHA/D95V**++) and experimental [13] structure parameters for FA-WA dimer. The internal coordinates are presented in Figure 1.

Int. Coord.	This work	Exp.
r_{HO} ($\text{H}_{\text{FA}}-\text{O}_{\text{WA}}$), Å	2.03864	2.03
r_{OH} ($\text{O}_{\text{FA}}-\text{H}_{\text{WA}}$), Å	2.11489	1.99
β_1 (Deg.)	108.995	107
β_2 (Deg.)	143.207	143.3

The experimental values presented by Lovas et al. [13] and our calculated values using D95V++** basis set at the MP2-CHA level are compared in Table IV. We found very good agreement between the calculated and the experimental values in the case of r_{OH} (the bond between the oxygen atom of formamide and the hydrogen atom of water) and the β_1 and the β_2 geometry parameters, whereas r_{HO} (the bond between the oxygen atom of water and the hydrogen atom of formamide) shows a 0.12 Å difference. This discrepancy was also reported by Jasien and Stevens [50].

In Table V we present the calculated intermolecular interaction energies obtained for the FA-WA complex using a geometry optimization technique in the given basis, considering the given methods (uncorrected, CHA, and CP) and levels of theory (RHF and MP2). The binding energy obtained by Engdahl et al. [14] is 8.25 kcal/mol, which agrees well with our BSSE-corrected the values calculated at the MP2 level using the CHA (8.211 for 6-31++G** and 8.277 for D95V**++) and CP (9.005 for 6-31++G** and 8.680 for D95V**++) schemes.

TABLE V

Interaction energies (in kcal/mol) for different FA–WA dimer geometries computed at the HF and second-order Møller–Plesset perturbation theory (Uncorr., CHA, CP) level, using D95V, D95V**, D95V++**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	D95V		D95V**		D95V++**		6-31G		6-31G**		6-31++G**	
	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2
Uncorr.	-12.012	-13.393	-8.429	-11.318	-7.948	-10.761	-12.926	-14.309	-9.879	-13.229	-8.265	-10.727
CHA	-11.258	-11.502	-7.861	-9.296	-7.474	-8.277	-11.594	-11.262	-8.101	-9.142	-7.779	-8.211
CP	-11.150	-11.067	-7.718	-8.891	-7.528	-8.680	-11.083	-10.630	-7.679	-8.796	-7.839	-9.005

4.2. HARMONIC AND ANHARMONIC VIBRATIONAL FREQUENCY

Formamide–Formamide Dimer

The FA–FA dimer has 30 vibrational normal modes from among which 24 (12 for each monomer) vibrations are characteristic to the monomer-type vibrational motion and 6 normal modes have an intermolecular character. In Table VI we present the conventional, CHA-, and CP-corrected results

at both the HF and MP2 levels for the intermolecular harmonic vibrational frequencies (ω_4^{int} , ω_5^{int} , ω_6^{int}) of the FA–FA dimer. The ω_4^{int} normal mode is symmetric angle bending where, in the course of vibrational motion, α_{NHO} and its symmetric pair increase and the α_{HOC} and its symmetric pair decrease; the ω_5^{int} normal mode is symmetric bond stretching of the two r_{HO} distance; and the ω_6^{int} normal mode is asymmetric bond stretching of both r_{HO} bonds.

TABLE VI

In-plane intermolecular frequencies for the FA–FA dimer computed at the HF and second-order Møller–Plesset perturbation theory (Uncorr., CHA, CP) level, using D95V, D95V**, D95V++**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	Method	ω_3 (cm ⁻¹)		ω_4 (cm ⁻¹)		ω_6 (cm ⁻¹)	
		RHF	MP2	RHF	MP2	RHF	MP2
D95V (66)	Uncorr.	148.5	148.3	184.3	189.8	212.2	224.8
	CHA	119.2	120.3	174.2	170.6	190.3	196.3
	CP	135.4	119.8	173.4	169.9	198.4	186.7
D95V** (120)	Uncorr.	132.8	141.4	154.7	176.8	186.8	221.8
	CHA	134.1	130.1	151.6	159.8	187.3	204.1
	CP	133.3	130.9	149.6	159.1	181.9	195.4
D95V++** (150)	Uncorr.	131.4	139.8	148.3	172.7	179.1	215.8
	CHA	129.6	122.2	146.3	151.9	175.5	186.0
	CP	129.4	124.5	144.1	151.3	175.1	188.8
6-31G (66)	Uncorr.	142.4	145.5	181.7	183.8	214.6	222.4
	CHA	134.3	129.5	182.8	179.6	215.2	223.9
	CP	141.2	125.5	175.4	166.1	208.5	201.9
6-31G** (120)	Uncorr.	136.6	147.1	160.7	177.4	195.7	223.1
	CHA	129.7	123.9	159.3	168.0	202.5	213.0
	CP	130.0	122.8	150.2	160.0	179.8	200.8
6-31++G** (150)	Uncorr.	134.0	136.4	154.4	171.8	186.1	212.6
	CHA	131.5	127.3	153.3	154.3	184.4	192.2
	CP	131.2	126.8	150.0	155.7	181.8	193.5
Exp. ¹		146		171		212	

The number of basis functions are given in parentheses.

¹ Ref. [12].

TABLE VII

Intermolecular frequencies for the FA-WA dimer computed at the HF and second-order Møller-Plesset perturbation theory (Uncorr., CHA, CP) level, using D95V, D95V**, D95V++**, 6-31G, 6-31G**, and 6-31++G** basis sets.

Basis	Method	ω_4 (cm ⁻¹)		ω_5 (cm ⁻¹)		ω_6 (cm ⁻¹)	
		RHF	MP2	RHF	MP2	RHF	MP2
D95V (46)	Uncorr.	205.2	210.4	520.9	512.7	611.3	555.6
	CHA	198.6	195.6	510.2	483.3	611.0	552.5
	CP	199.0	200.7	515.7	492.6	611.5	555.8
D95V** (85)	Uncorr.	175.7	210.8	342.6	344.7	404.5	414.8
	CHA	174.2	192.1	361.5	350.2	424.3	446.3
	CP	171.6	181.7	360.3	351.5	430.9	452.7
D95V++** (106)	Uncorr.	169.8	233.6	336.7	374.6	399.7	440.0
	CHA	163.3	194.8	348.1	381.0	426.1	440.6
	CP	164.7	196.4	347.0	386.5	430.1	458.3
6-31G (46)	Uncorr.	210.3	219.0	522.7	445.2	604.7	547.2
	CHA	213.5	211.1	508.2	468.4	605.4	546.9
	CP	203.8	205.6	513.1	477.1	607.2	547.3
6-31G** (85)	Uncorr.	217.0	249.8	338.2	355.0	431.7	425.4
	CHA	189.1	199.7	380.1	388.8	422.6	414.8
	CP	179.5	196.4	384.8	396.3	447.8	414.8
6-31++G** (106)	Uncorr.	177.8	189.9	386.6	352.1	425.3	423.7
	CHA	177.1	186.9	405.8	371.6	432.9	437.4
	CP	176.8	189.9	405.3	369.8	437.5	457.7
Exp. ¹		185.4		386		416.6	

The number of basis functions are given in parentheses.

¹ Ref. [14].

Usually the vibration frequencies of molecular complex are evaluated at the harmonic approximation applying the Wilson F-G analysis and using the BSSE-uncorrected Hessians. On the other hand, the vibrational frequencies, in particular there with an intermolecular character, contain considerable anharmonic effects and therefore it is difficult to follow these two important corrections in a distinct way. Nevertheless, it can be noted that frequencies with BSSE corrections generally draw near to the experimental values. Furthermore, in the case of the ω_4^{int} normal mode we found that the uncorrected MP2 contribution increases, while the BSSE-corrected CHA and CP schemes decrease, the HF frequency values. At the same time, the full CP-corrected MP2 intermolecular frequency values (Table VIII) are close to those obtained by considering only the intermolecular coordinate as the geometry parameters (Table VII).

Considering the monomer-type vibrations (Table VIII) it can be found that two different dimer frequencies correspond to the similar monomer vibrations, but their values are usually shifted (mostly blue-shifted, but red shifts can also be found in the case of

ω_1^{FA} and ω_2^{FA}) due to the intermolecular interaction. Taking in to account the full CP-corrected values in the dimer calculations, we found another frequency shift, but in this case due to the BSSE effects. Moreover, the frequency values show an important basis size effect at the MP2 level, which implies the shifts in dimer frequency values will change.

The results of the anharmonic frequency corrections show a more complex picture. Because of the large numbers of the anharmonic frequencies in Table VIII only the diagonal elements of anharmonic frequency matrix are presented. The most important effect in the anharmonic values is given by the influence of the adjacent molecule, which generates substantial shifts in the anharmonicity of different monomer normal modes within the dimer system. Although the above-mentioned "cluster" effect is quite uniform, the basis size effects become much more complicated. In the case of hydrogen bond stretching (N—H, C—H) and angle-bending vibrations, changes in the anharmonic frequency are not so important, but the torsion angle and C=O stretching modes show very dissimilar re-

TABLE VIII

The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of FA-FA dimer computed at MP2 level of theory, using 6-31G and 6-31++G** basis sets.

No.	ν^{dim}	ν^{CP}	ν^{mon}	$\chi_{\text{ii}}^{\text{dim}}$	$\chi_{\text{ii}}^{\text{CP}}$	$\chi_{\text{ii}}^{\text{mon}}$	ν^{dim}	ν^{CP}	ν^{mon}	$\chi_{\text{ii}}^{\text{dim}}$	$\chi_{\text{ii}}^{\text{CP}}$	$\chi_{\text{ii}}^{\text{mon}}$	Assign.
Formamide													
6-31G							6-31++G(d, p)						
1	3705.5	3711.2	3763.1	-33.3	-32.5	-41.580	3770.0	3770.3	3814.1	-32.5	-32.4	-40.513	N-H a.
	3705.2	3710.8		-33.8	-33.1		3769.9	3770.1		-32.9	-32.8		
2	3425.2	3455.1	3615.6	-45.0	-41.1	-37.226	3465.8	3467.5	3660.9	-49.9	-49.2	-36.047	N-H s.
	3381.3	3420.1		-53.0	-47.2		3424.8	3426.4		-58.9	-57.8		
3	3081.2	3072.3	3060.2	-35.3	-35.5	-72.859	3103.9	3104.2	3083.9	-33.0	-33.0	-67.715	C-H
	3077.9	3069.3		-35.4	-35.7		3101.6	3101.9		-33.1	-33.1		
4	1793.4	1778.6	1731.6	1.6	3.1	-7.396	1795.5	1796.4	1794.9	-24.0	-24.4	-6.634	C=O
	1768.4	1760.5		1.4	2.8		1773.9	1774.4		-22.3	???		
5	1695.4	1697.5	1680.2	-1.6	-2.2	-3.401	1677.0	1677.2	1654.2	-9.5	-9.4	-8.544	H-N-H
	1653.8	1662.3		-1.6	-1.6		1666.6	1667.9		-3.9	-4.0		
6	1446.9	1448.1	1444.9	-2.9	-3.1	-6.791	1444.0	1446.7	1444.0	-3.8	-3.9	-9.119	O=C-H
	1445.2	1446.7		-3.0	-3.1		1444.8	1445.8		-3.9	-3.9		
7	1367.3	1354.5	1297.5	-2.9	-2.8	-5.314	1367.7	1367.4	1295.9	-2.9	-2.8	-4.974	C-N
	1352.1	1342.7		-2.6	-2.6		1353.1	1352.4		-2.6	-2.6		
8	1125.6	1117.5	1074.7	-0.9	-0.9	-1.448	1112.1	1111.6	1075.2	-0.8	-0.8	-1.283	C-N-H
	1121.1	1113.7		-0.8	-0.8		1106.0	1105.6		-0.7	-0.7		
9	1071.1	1060.4	1033.4	-2.2	-1.6	-2.252	1060.2	1067.7	1041.0	0.5	-1.1	-1.302	O of P
	1049.5	1047.7		-1.2	-1.1		1046.2	1056.1		1.1	-0.7		
10	936.0	906.8	639.2	-4.8	-6.2	-37.968	824.3	827.8	628.1	-15.5	-20.7	-15.897	Torsion
	905.5	864.1		-7.1	-8.1		785.1	789.7		-6.5	-8.3		
11	631.1	616.6	563.9	-0.6	-0.4	1.103	622.8	621.2	565.6	-0.6	-0.6	1.249	O=C-N
	607.3	599.3		0.2	0.3		605.7	604.8		-0.2	0.3		
12	579.1	565.0	459.8	1.5	7.4	15.410	413.9	425.5	276.1	17.8	12.9	-462.7	Torsion
	577.4	563.4		1.4	-0.7		394.5	404.4		28.2	24.8		
Intermolecular													
1	158.9	154.8		-0.2	-0.5		47.5	118.3		451.2	47.6		O of P
2	145.8	133.1		-0.4	-0.1		29.6	99.7		2101	11.0		O of P
3	70.2	66.4		0.03	-0.2		9.2	49.0		16,800	1.5		O of P
4	228.2	216.0		-2.8	-3.2		171.8	176.2		-3.1	-2.3		H...O
5	222.9	201.8		-0.5	-1.2		212.6	217.3		-1.8	-1.2		H...H
6	184.2	166.9		-1.2	-1.9		136.4	136.2		-0.2	-0.1		O...O

sults. Considering the full CP-corrected BSSE-free anharmonic frequency calculations, no major corrections can be found for the monomer-type vibrations, which in practice means that their effects could be generally neglected for the FA-FA dimer. Regarding the intermolecular normal modes, in addition to the "cluster" and basis size effects, the BSSE corrections become very important, especially for "out of plane" normal modes (see MP2/6-31++G**). After these, considering the collective effects of basis size and BSSE corrections on the intermolecular vibration frequencies, it can be concluded that major corrections are obtained in the cases of the harmonic approximation given by the quality (applying polarization and diffuse basis sets) and the BSSE of the applied basis sets, which is

followed by the similar correction of the anharmonic approximation.

Formamide-Water Dimer

Besides the six intermolecular normal modes, 15 (12 for FA and 3 for WA monomer) normal-mode vibrations with monomer character can be identified. The conventional, CHA-, and CP-corrected results (optimized with the intermolecular parameters) at both the HF and MP2 levels and their proposed experimental assignment for the intermolecular harmonic vibrational frequencies (ω_4^{int} , ω_5^{int} , ω_6^{int}) of the FA-WA system are given in Table VII. The assignment of these experimental values in the far-infrared region, where the intermolecular fun-

amentals are expected, is difficult because a relatively large number of bands can be observed. According to Engdahl et al. [14], the ω_4^{int} frequency is identified as an intermolecular stretching vibration, ω_5^{int} is considered to be a water-in-plane libration, ω_6^{int} is an out-of-water-plane libration. The frequency results show that these values have an important MP2 perturbational correction but the BSSE effects also could not be neglected. As we noted in the case of the system, the anharmonic correction plays an important role in comparing the calculated values with experimental values.

Comparing the monomer-type vibrational normal modes of the FA-WA with those in FA and WA monomers, we observe similar effects to the previous system. Considerable frequency shifts (blue or red shift) can be found resulting from interaction with the adjoining molecule, but of course the magnitudes of these shifts differ in comparison with the FA-FA system. At the same time, the basis size effects are also relevant: the most affected normal modes (Table IX) are the torsion modes (ω_{10}^{FA} and ω_{12}^{FA}) of the FA monomer, the ω_2^{WA} of the WA monomer, and all six intermolecular vibrations ($\omega_1^{\text{int}}-\omega_6^{\text{int}}$).

Considering the anharmonic corrections, similar effects can be observed than as in the previous FA-FA system. The most important anharmonic shifts are obtained, in general, for the H-X ($X=C, N, O$) stretching normal modes ($\omega_1^{\text{FA}}, \omega_2^{\text{FA}}, \omega_3^{\text{FA}}, \omega_1^{\text{WA}}, \omega_2^{\text{WA}}$), where the correction could have values between 55 and 100 cm^{-1} , while their BSSE effects can reach 10% at most from the anharmonic frequency. A considerable difference between the 6-31G and 6-31++G** results in the anharmonic frequency is obtained for the dimer system. The most typical case is found for x_{44} (C=O stretching mode), where the 6-31G results show positive values for both the uncorrected (10.132 cm^{-1}) and the CP-corrected (15.942 cm^{-1}) levels, while the 6-31++G** values are negative. The BSSE correction in the 6-31++G** results is also important: -16.043 cm^{-1} at uncorrected level, and -8.822 cm^{-1} for the CP-corrected level. With respect to the intermolecular normal modes, the out-of-plane vibration with low frequencies usually shows a very dissimilar and unrealistic anharmonic correction, especially for the MP2/8-31++G** CP-corrected case. This phenomenon may be related to many facts: i) in the CP method the PES is very flat, the intermolecular force constants are very small [21], and the numerical calculations could give significant errors; ii) the role of the well-balanced basis set is very important, therefore we consider that the

6-31++G** does not give us adequate results. For example, the 6-31++G(2d, 2p) basis set could be a more suitable choice, but the available computer capacity does not allow us to perform such full-CP anharmonic calculations.

5. Conclusions

Our BSSE-free studies for hydrogen-bonded systems have included the formamide-formamide and formamide-water dimers. The overall BSSE-free ab initio results agree satisfactorily with the experimental values, especially in the case of geometrical parameters and binding energies. For intermolecular harmonic and anharmonic vibrational frequencies we obtained a systematic BSSE correction. It can also be mentioned that the BSSE correction of the potential energy surface does not induce radical changes in the molecular symmetry of the FA-FA and FA-WA dimers. Further, we note that the agreement between the CHA- and CP-corrected results at both the HF and correlated (MP2) levels are very good. This observation is consistent with our previous studies in the field of intermolecular interactions. Similar to our earlier results, the difference between the uncorrected and corrected values become smaller for large enough basis sets as the values of the intermolecular interactions converge to each other. But, considering the correlated level, the amount of BSSE in the intermolecular interaction energies is much larger than that at the HF level, and this effect is also conserved in the values of the force constants and harmonic vibrational frequencies. All these results clearly indicate the importance of the proper BSSE-free correlation treatment with the well-defined basis functions. Considering the harmonic and anharmonic frequency results, especially for the intermolecular normal modes, we conclude that the BSSE corrections of the harmonic approximation are much more important than the anharmonic corrections. At the same time, in certain normal modes the BSSE effects of the anharmonic frequencies could give important corrections. Finally, the out-of-plane vibrations of low frequencies require much more accurate numerical and quantum chemical treatment.

ACKNOWLEDGMENT

A. Bende thanks the European Union for a fellowship under contract No BMH4-CT96-1618, which funded his study visit to Heidelberg.

TABLE IX
The uncorrected and CP-corrected harmonic and diagonal anharmonic frequency of FA-WA dimer computed at the MP2 level of theory, using 6-31G and 6-31++G basis sets.**

No.	ν^{dim}	ν^{CP-dim}	ν^{mon}	χ_{ii}^{dim}	χ_{ii}^{CP-dim}	χ_{ii}^{mon}	ν^{dim}	ν^{CP-dim}	ν^{mon}	χ_{ii}^{dim}	χ_{ii}^{CP-dim}	χ_{ii}^{mon}	Assign.
6-31G													
Formamide													
1	3723.3	3725.6	3763.1	-62.304	-60.828	-41.580	3790.4	3798.1	3814.1	-55.301	-51.570	-40.513	N-H a.
2	3467.6	3491.8	3615.6	-57.131	-60.789	-37.226	3578.8	3604.7	3660.9	-57.889	-52.935	-36.047	N-H s.
3	3087.0	30769	3060.2	-71.188	-71.806	-72.859	3109.1	3106.2	3083.9	-66.641	-66.725	-67.715	C-H
4	1764.3	1767.7	1731.6	10.132	15.942	-7.396	1783.7	1787.3	1794.9	-16.043	-8.822	-6.634	C=O
5	1656.6	1662.9	1680.2	-2.556	-3.220	-3.401	1657.0	1664.1	1654.2	-6.523	-7.033	-8.544	H-N-H
6	1438.9	1443.1	1444.9	-5.434	-5.814	-6.791	1443.5	1444.9	1444.0	-7.842	-7.999	-9.119	O=C-H
7	1359.4	1351.2	1297.5	-5.458	-5.434	-5.314	1343.0	1338.6	1295.9	-5.155	-5.070	-4.974	C-N
8	1116.2	1112.5	1074.7	-1.523	-1.546	-1.448	1101.5	1095.8	1075.2	-2.020	-1.711	-1.283	C-N-H
9	1044.9	1045.5	1033.4	-2.295	-2.430	-2.252	1050.1	1050.7	1041.0	-1.093	-1.583	-1.302	O of P
10	866.2	848.6	639.2	-11.672	-8.555	-37.968	751.9	725.3	628.1	-9.720	-5.897	-15.897	Torsion
11	617.7	619.2	563.9	-55.960	-0.404	1.103	603.7	605.9	565.6	-1.710	-4.921	1.249	O=C-N
12	546.9	534.6	459.8	0.030	-23.704	15.410	352.1	281.7	276.1	-17.773	-15.348	-462.7	Torsion
6-31++G(d, p)													
Water													
1	3803.2	3826.3	3833.5	-79.279	-75.346	-55.815	3961.1	3976.4	4010.4	-76.728	-75.085	-49.236	O-H
2	3521.8	3552.3	3657.3	-63.485	-72.789	-47.968	3682.8	3720.5	3863.6	-98.877	-89.886	-44.047	O-H
3	1695.9	1696.4	1662.9	-23.446	-14.895	-22.853	1641.7	1641.9	1619.5	-18.019	-19.746	-17.130	H-O-H
Intermolecular													
1	680.6	570.2		-7.601	-10.784		628.9	578.5		-25.539	-58.125		O of P
2	193.3	182.1		-1.568	-1.900		215.5	97.4		-57.537	-65.707		O of P
3	128.5	154.3		-56.430	-0.973		124.6	78.2		-42.974	-145.493		O of P
4	446.6	488.5		-26.012	-14.001		423.7	417.8		-20.788	-24.875		O _{FA} -H _{WA} -O _{WA}
5	217.8	193.8		-5.474	-4.795		189.9	185.3		-4.689	-4.638		H _{WA} -O _{FA}
6	210.5	197.7		-5.070	-3.484		177.0	161.8		-4.301	-5.914		H _{FA} -O _{WA}

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