

# Basis set superposition error-counterpoise corrected potential energy surfaces. Application to hydrogen peroxide $\cdots X$ ( $X=F^-$ , $Cl^-$ , $Br^-$ , $Li^+$ , $Na^+$ ) complexes

Martha C. Daza,<sup>a)</sup> J. A. Dobado, and José Molina Molina<sup>b)</sup>

*Grupo de Modelización y Diseño Molecular, Instituto de Biotecnología, Campus Fuentenueva, Universidad de Granada, 18071-Granada, Spain*

Pedro Salvador and Miquel Duran

*Institut de Química Computacional, Universitat de Girona, 17071-Girona, Spain*

José Luis Villaveces

*Laboratorio de Investigaciones Básicas, Facultad de Ciencias, Universidad Nacional de Colombia, Santa Fe de Bogotá, Colombia*

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Møller–Plesset (MP2) and Becke-3-Lee-Yang-Parr (B3LYP) calculations have been used to compare the geometrical parameters, hydrogen-bonding properties, vibrational frequencies and relative energies for several  $X^-$  and  $X^+$  hydrogen peroxide complexes. The geometries and interaction energies were corrected for the basis set superposition error (BSSE) in all the complexes (1–5), using the full counterpoise method, yielding small BSSE values for the 6-311+G(3df,2p) basis set used. The interaction energies calculated ranged from medium to strong hydrogen-bonding systems (1–3) and strong electrostatic interactions (4 and 5). The molecular interactions have been characterized using the *atoms in molecules theory* (AIM), and by the analysis of the vibrational frequencies. The minima on the BSSE-counterpoise corrected potential-energy surface (PES) have been determined as described by S. Simón, M. Duran, and J. J. Dannenberg, and the results were compared with the uncorrected PES. © 1999 American Institute of Physics. [S0021-9606(99)30924-7]

## I. INTRODUCTION

Hydrogen peroxide (HP) plays an important role in many fields such as atmospheric chemistry,<sup>1</sup> oxidation reactions,<sup>2,3</sup> and biological processes.<sup>4</sup> Theoretical studies of HP complexes have been reported in the literature, including HP dimer,<sup>5–7</sup> HP  $\cdots$  water,<sup>8,9</sup> HP  $\cdots$  hydrogen halides,<sup>10</sup> and recently HP  $\cdots$  urea<sup>11</sup> complexes. These studies have been performed mainly by the supermolecule method using the basis set superposition error (BSSE) correction by the counterpoise method (CP).<sup>12,13</sup>

Until now, the CP correction has been done only with uncorrected equilibrium geometry, except in complexes where only one intermolecular parameter was needed for the definition of the system.<sup>14</sup> However, a method for calculating the BSSE-counterpoise corrected potential-energy surface (PES) has been proposed recently by S. Simón, M. Duran, and J. J. Dannenberg.<sup>15</sup>

The determination of the interaction energy for weakly bonded systems is estimated mostly within the so-called supermolecular approach, whereby the interaction energy is calculated as the energy difference between the whole system and its subunits. However, the use of finite basis sets centered on the nuclei and, in essence, the linear combination

of atomic orbitals-molecular orbitals (LCAO-MO) formalism, leads to the BSSE. As pointed out many years ago,<sup>12,13</sup> the intramolecular description of the fragments within the supermolecule can be improved with the basis functions of the partner, while this is not possible in the description of the isolated fragments. The main consequence is that the interaction energy is artificially overestimated. However, effects on the molecular geometry<sup>16–18</sup> or on the electronic density<sup>19</sup> can be important and should be taken into account. In recent years, great effort has been made to avoid or minimize the BSSE. There are two different ways to face the problem, *a priori* and *a posteriori*. The former consists of constraining the supermolecule description in order to keep it consistent with its fragments. Several recipes have been proposed such as the constrained dimer function method,<sup>20</sup> by Andrzej J. Sadlej, or the chemical Hamiltonian approach (CHA),<sup>21</sup> introduced by István Mayer. The CHA theory for intermolecular interactions<sup>22–26</sup> eliminates the purely BSSE terms of the Hamiltonian that make the BSSE possible and therefore BSSE-free descriptions, including electronic density, to be potentially determined at any level of theory.<sup>24–26</sup> On the other hand, there are different approaches that restrict the MO of each fragment within the supermolecule in its own basis sets, resulting in the discarding of the charge-transfer terms.<sup>27,28</sup> Moreover, the most widely used way to handle BSSE has been the full counterpoise method, introduced by Jansen–Ross and Boys–Bernardi,<sup>12,13</sup> which is based on the assumption that the error is minimized if the same basis set is

<sup>a)</sup>Present address: Laboratorio de Investigaciones Básicas, Facultad de Ciencias, Universidad Nacional de Colombia, Santa Fe de Bogotá, Colombia.

<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: jmolina@goliat.ugr.es

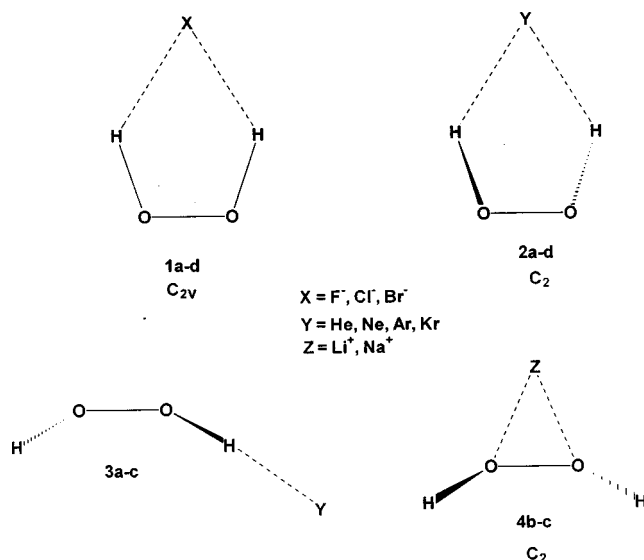


FIG. 1. Hydrogen peroxide HPX complexes 1–5 studied.

used for the description of both the supermolecule and its fragments. Although the validity of this approach has been discussed for many years,<sup>29,30</sup> recent calculations have shown that full counterpoise converge with CHA results, and therefore reliable results for intermolecular complexes can be achieved,<sup>31</sup> and its usefulness has recently been established.<sup>29,30,32</sup>

For all the HP complexes investigated by our group, the BSSE was corrected by the CP method,<sup>12,13</sup> at the Hartree–Fock (HF), Møller–Plesset (MP2), or density-functional theory (DFT). No PESs have previously been reported for the complexes studied in this work. However, PESs have been studied accurately for such related systems as water·halogen<sup>33,34</sup> and water·alkali ions.<sup>34</sup>

In this work, the HP·X complexes (HPX), structures 1–5 have been used as a suitable test for the BSSE-counterpoise corrected and noncorrected PESs comparison, in order to demonstrate the utility of obtaining the counterpoise corrected PESs (see Fig. 1).

The MP2 level has been used together with DFT method, the utility of which has been demonstrated for the description of the physical and chemical molecular properties,<sup>35–40</sup> including hydrogen-bond systems.<sup>41–44</sup>

## II. BSSE-COUNTERPOISE CORRECTED PES

Let us consider a supermolecule  $AB$ , made up of two interacting systems  $A$  and  $B$ . Within the supermolecular approach, the interaction energy can be expressed as

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

where  $E_Y^Z(X)$  represents the energy of system  $X$  at geometry  $Y$  with basis set  $Z$ . The description of system  $A$  and  $B$  in the supermolecule can be improved with the basis functions of system  $B$  and  $A$ , respectively, whereas no extension of the basis is possible in the second and third terms. Thus, Eq. (1) is BSSE-polluted. Following the counterpoise receipt, the interaction energy should be expressed as

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

Equations (1) and (2) will converge when a complete basis set is used. However, Eq. (2) can be applied only if the nuclear configurations of the subsystems are frozen within the supermolecule, e.g., when the relaxation of the subsystems is not possible. This is due to the arbitrariness of the position of the basis functions belonging to the partner. To avoid this inconsistency, we can rewrite Eq. (1) as

$$\Delta E(AB) = [E_{AB}^{AB}(AB) - E_{AB}^A(A) - E_{AB}^B(B)] + [E_{AB}^A(A) - E_A^A(A) + E_{AB}^B(B) - E_B^B(B)]. \quad (3)$$

The interaction energy is partitioned into an electronic contribution (first term) and a positive definite relaxation contribution (second term). According to the Boys–Bernardi approach, only the first term must be corrected, as the same basis set is used in the relaxation term for each subsystem. Thus, the counterpoise corrected interaction energy should be written as

$$\Delta E^{CP}(AB) = [E_{AB}^{AB}(AB) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B)] + [E_{AB}^A(A) - E_A^A(A) + E_{AB}^B(B) - E_B^B(B)], \quad (4)$$

or, as is usual in the literature

$$\Delta E^{CP}(AB) = [E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B)] + [E_{AB}^A(A) - E_{AB}^{AB}(A) + E_{AB}^B(B) - E_{AB}^{AB}(B)] = \Delta E(AB) + \delta_{AB}^{BSSE}, \quad (5)$$

where the counterpoise correction expressed as  $\delta_{AB}^{BSSE}$  depends on the structure parameters of the supermolecule, as indicated by the subscript  $AB$ . Thus, BSSE is not an additive term to interaction energy; instead, it must be taken into account when computing interaction energies at each point on the PES. An easy way to account for the BSSE effects on geometry is to define the counterpoise corrected PES<sup>15</sup> for the supermolecule as

$$E^{CP}(AB) = E_{AB}^{AB}(AB) + [E_{AB}^A(A) - E_{AB}^{AB}(A) + E_{AB}^B(B) - E_{AB}^{AB}(B)] = E(AB) + \delta_{AB}^{BSSE}. \quad (6)$$

The equation above shows that the counterpoise correction should be more generally applied to the supermolecule description, instead of to the interaction energy.  $N$ -order derivatives can easily be calculated as a linear combination of the contributions of each term, as described by S. Simón, M. Duran, and J. J. Dannenberg.<sup>15</sup> Any property to be expressed as derivative of the energy can be calculated. However, no counterpoise-corrected electronic density exists for the supermolecule. The energy of the supermolecule depends upon its partitioning. That is, if we consider the molecule as a whole, then no counterpoise correction can be applied. With respect to intermolecular complexes, in the interest of consistency, we can define as many fragments as molecules that make up the complex. In this way, we can determine supermolecule structures and energies that are consistent with the previously defined fragments. On the contrary, we can consider the molecule to be made up of a set of atoms, which is

TABLE I. Geometrical parameters<sup>a</sup> (Å and degrees) for HPX complexes (1–5) and HP monomer, at the different theoretical levels.

	B3LYP/6-311+G(3df,2p)			MP2(full)/6-311+G(3df,2p)		
	1 HP··F <sup>-</sup>	2 HP··Cl <sup>-</sup>	3 HP··Br <sup>-</sup>	1 HP··F <sup>-</sup>	2 HP··Cl <sup>-</sup>	3 HP··Br <sup>-</sup>
O–O	1.470(1.473)	1.460(1.460)	1.459(1.458)	1.467(1.469)	1.456(1.455)	1.454(1.453)
O–H	1.000(1.000)	0.986(0.986)	0.984(0.984)	0.999(0.997)	0.985(0.983)	0.983(0.981)
X··H	1.636(1.641)	2.199(2.205)	2.381(2.386)	1.618(1.647)	2.141(2.182)	2.305(2.353)
∠O–O–H	95.5(95.6)	99.7(99.8)	100.6(100.6)	94.8(95.4)	98.8(99.2)	99.7(100.0)
∠H··X··H	61.1(61.0)	48.1(48.1)	44.9(44.9)	60.6(60.2)	48.5(47.9)	45.5(44.8)
∠X··H–O	144.0(143.9)	146.2(146.2)	146.9(146.9)	144.9(144.5)	146.9(146.8)	147.6(147.6)
	4	5		4	5	
	HP··Li <sup>+</sup>	HP··Na <sup>+</sup>		HP··Li <sup>+</sup>	HP··Na <sup>+</sup>	
O–O	1.453(1.453)	1.450(1.450)		1.449(1.447)	1.444(1.444)	
O–H	0.973(0.973)	0.971(0.971)		0.971(0.970)	0.969(0.968)	
X··O	1.939(1.942)	2.326(2.334)		1.951(1.971)	2.332(2.359)	
∠O–O–H	103.3(103.3)	103.0(103.0)		102.4(102.4)	102.2(102.1)	
∠O··X··O	44.0(43.9)	36.3(36.2)		43.6(43.1)	36.1(35.6)	
∠HOOH	101.0(100.2)	95.4(95.1)		102.0(100.8)	96.4(95.5)	
	HP			HP		
O–O	1.446			1.441		
O–H	0.966			0.963		
∠O–O–H	100.9			100.1		
∠HOOH	112.0			111.8		

<sup>a</sup>In parentheses the corresponding values for the BSSE-counterpoise corrected PES.

physically true. From this perspective, the correction would be independent of any chemical partitioning of the molecule and the BSSE can be seen as an intramolecular property, as defined in the CHA method. For molecular complexes, chemical background usually helps us to define the fragments. However, in case of chemical reactions this is not an simple task.<sup>45</sup>

### III. COMPUTATIONAL METHODS

All the calculations have been carried out using the GAUSSIAN 94 and GAUSSIAN 98 package<sup>46,47</sup> of programs, using the 6-311+G(3df,2p) basis set. DFT methodology has been applied through the B3LYP hybrid exchange-correlation functional.<sup>48,49</sup> Given that for the studied complexes there is a small amount of core electrons, MP2 (full) all electron calculations were performed taking into account that for the basis set used the correlated electrons are mainly the valence ones. The stationary points were optimized, bearing in mind the symmetry restrictions ( $C_{2v}$  for 1–3 and  $C_2$  for 4 and 5) characterized by vibrational analysis (no imaginary frequencies for minima). Further optimizations of the minima without symmetry restrictions yielded the same structures. In addition, BSSE was estimated using the full counterpoise method,<sup>12,13</sup> as described elsewhere.<sup>5,10</sup>

BSSE-counterpoise corrected geometry optimizations using internal coordinates was carried out as described by S. Simón, M. Duran, and J. J. Dannenberg<sup>15</sup> with some modifications. The energy and gradients with respect to the geometrical parameters were calculated for the complex, monomers, and monomers in the whole basis set (ghost orbitals), at every point using GAUSSIAN 98 package.<sup>47</sup> BSSE-counterpoise corrected PESs were constructed as shown elsewhere.<sup>15</sup> For the location of the minimum geometries, Pulay's direct inversion in the iterative subspace (DIIS)<sup>50</sup>

with the Broyden–Fletcher–Goldfarb–Shanno (BFGS)<sup>51</sup> updating procedure for the inverse Hessian was implemented. Initial guess for the inverse Hessian proved essential for the optimization procedure. Uncorrected initial inverse Hessian was determined from HF/3-21G frequency calculations. The convergence criteria was set at  $10E^{-5}$  a.u. in the root-mean-squared (rms) of the gradient. This mixed DIIS-variable metric (DIIS-VM) scheme proved highly efficient and 4–6 cycles were necessary to reach the desired convergence. The analytic Cartesian second-derivative matrix was computed for the complex and monomer with and without ghost orbitals at the BSSE-counterpoise corrected minimum geometry.

Bader analyses were performed with the AIMPAC program series<sup>52</sup> using the B3LYP wavefunction as input, as described in the AIM theory.<sup>53,54</sup> A brief overview of the AIM terminology is explained elsewhere.<sup>55,56</sup> Graphic representations for the  $\rho(r)$  and  $\nabla^2\rho(r)$  contour plots were made with the MORPHY program.<sup>57</sup>

### IV. RESULTS AND DISCUSSION

Calculations were performed for the HPX complexes 1–5 (see Fig. 1), the X ligand goes from F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> anions to alkaline cations, with large metal oxygen electrostatic interactions, Li<sup>+</sup> and Na<sup>+</sup>.

For complexes 1–5, different configurations were tested on the PES, and all the stationary points found, on the HPX complexes PES, showed only cyclic minima. Those with  $C_{2v}$  symmetry showed HP as hydrogen donor (1–3), and, those with  $C_2$  symmetry showed HP as the oxygen donor (4 and 5), see Fig. 1.

#### A. Geometrical parameters

The geometrical parameters found for the stationary points were presented in Table I together with the HP mono-

TABLE II. Charge density,  $\rho(r)$ , Laplacian of the charge density,  $\nabla^2\rho(r)$ , geometrical parameters for the hydrogen bonds, ellipticity,  $\epsilon$ , and local energy density,  $E_d(r)$ , for the BCPs and RCPs on the HPX complexes **1–5**, at the B3LYP/6-311+G(3df,2p) level.

Complexes	Description	$\rho(r)$ ( $e/a_0^3$ )	$\nabla^2\rho(r)$ ( $e/a_0^5$ )	Dist. (Å)	Angle (deg)	$\epsilon$	$E_d(r)$ (hartree/ $a_0^3$ )
<b>1</b>	(3,-1) Bond (H··F)	0.0543	0.0160	1.636	144.0	0.0275	-0.0078
	(3,1) Ring	0.0311	0.0166				0.0033
<b>2</b>	(3,-1) Bond (H··Cl)	0.0277	0.0650	2.199	146.2	0.0526	-0.0015
	(3,1) Ring	0.0187	0.0727				0.0013
<b>3</b>	(3,-1) Bond (H··Br)	0.0232	0.0512	2.381	146.9	0.0621	-0.0007
	(3,1) Ring	0.0163	0.0574				0.0009
<b>4</b>	(3,-1) Bond (O··Li)	0.1050	0.9737	1.939	44.0	0.2721	0.0062
	(3,1) Ring	0.0883	0.8369				0.0130
<b>5</b>	(3,-1) Bond (O··Na)	0.0692	0.5777	2.326	36.3	0.1802	0.0105
	(3,1) Ring	0.0575	0.4896				0.0137

mer ones, at the different levels studied. As described above, the only stationary points for the complexes **1–5** studied were cyclic ones.

Complexes **1–3** were planar with  $C_{2v}$  symmetry in which the torsional  $\angle\text{HOOH}$  angle became  $0^\circ$ . Both levels yielded very similar geometrical parameters for **1–3**. The main difference appeared for the  $\text{X}\cdots\text{H}$  hydrogen-bond length, with a maximum value of  $0.076$  Å for **3**, the MP2 values consistently giving shorter hydrogen bonds.

The overall geometry for the HP within the different complexes **1–3** showed the following trend compared with the HP at the same level. The O–O bond lengths were greater in the complexes, the deviation becoming longer as the  $\text{X}^-$  anion became smaller. The same trend was detected in the O–H bonds. This characteristic was compatible with larger electron donation to the hydrogen bond when the  $\text{X}^-$  anion became smaller (larger electron-density concentration).

The  $\angle\text{OOH}$  angles decreased upon the formation of the complexes, due to the strength of the two hydrogen bonds, increasing also with the  $\text{X}^-$  size (see Table I). Complexes **1–3**, formed two hydrogen bonds between  $\text{X}^-$  and both hydrogens of HP. The hydrogen-bond geometries were compatible with strong ones, giving the  $\angle\text{X}\cdots\text{H}-\text{O}$  angle  $\sim 146^\circ$  at both levels.

In complexes **4** and **5**, X was the alkaline cations  $\text{Li}^+$  and  $\text{Na}^+$ , respectively. In both cases, only cyclic structures ( $C_2$  symmetry) were found as stationary points on the PES. Moreover, both complexes showed interactions with both oxygens. The geometry of the HP moiety in **4** and **5** remained almost unchanged compared with the HP monomer at the same level. The main difference was found for the  $\angle\text{HOOH}$  torsion angle (i.e.,  $\sim 101^\circ$  and  $95^\circ$  for **4** and **5**, respectively).

The behavior of the interactions in **1–5** have been analyzed using the AIM methodology. In Table II, characteristics of the numerical values of the critical points were tabulated for **1–5** complexes. Moreover, Figs. 2 and 3 depict  $\rho(r)$  or  $\nabla^2\rho(r)$  contour plots for **1–3** and **4, 5** complexes, respectively.

The cyclic nature for complexes **1–5** was confirmed by a corresponding ring critical point (RCP). This RCP was characterized both graphically [by asterisk (\*) in Figs. 2 and 3] and numerically (see Table II).

Complexes **1–3** presented two hydrogen bonds, and their corresponding bond critical point (BCP) was determined. The  $\rho(r)$  values at the BCP were higher than in other hydrogen-bonded complexes of HP.<sup>58</sup> Compatible with

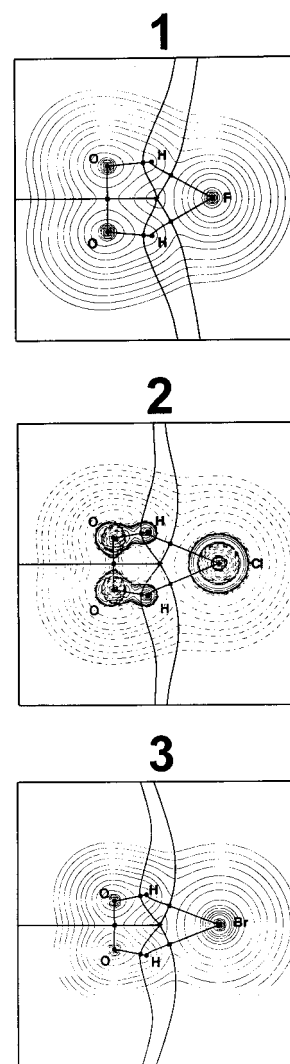


FIG. 2.  $\rho(r)$  and  $\nabla^2\rho(r)$  contour maps for complexes **1–3**, in the molecular plane obtained using the MORPHY program (Ref. 57).

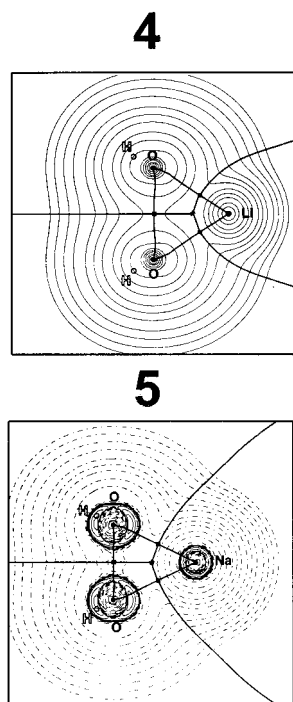


FIG. 3.  $\rho(r)$  and  $\nabla^2\rho(r)$  contour maps for complexes **4** and **5**, in the molecular plane obtained using the MORPHY program (Ref. 57).

higher  $\Delta E^{cp}$  values listed in Table III. For **1–3**, the local energy density,  $E_d(r)$ , were small but negative, indicating a weak electron delocalization in the bond (very small covalent character). Generally, the hydrogen-bond interactions remained almost of electrostatic nature. The interaction in **4** and **5** was somewhat different, giving two BCPs between the metal cation and both oxygens. This interaction showed mainly an ionic type. The  $\rho(r)$  values were small and  $\nabla^2\rho(r)$  values large and positive. In addition,  $E_d(r)$  became small and also positive. In Figs. 2 and 3 the  $\rho(r)$  or  $\nabla^2\rho(r)$  contour plots were represented for **1–3** and **4, 5**, showing the different type of interaction for the HPX complexes. The hydrogen-bond interaction shows the disposition of a maxima  $-\nabla^2\rho(r)$  in  $\text{Cl}^-$  towards  $\nabla^2\rho(r)$  minima in the hydrogens. On the other hand, the positive  $\nabla^2\rho(r)$  region on  $\text{Na}^+$  is directed towards the maxima in  $-\nabla^2\rho(r)$  on the oxygens (electron pairs).

## B. Interaction energies and BSSE

The total energies of the HPX complexes and monomers studied were summarized in Table SI-I, available as Supplementary material. The corresponding binding energy (on the uncorrected PES), corrected and uncorrected for the BSSE together with the BSSE are listed in Table III, at the two levels used. The calculations were performed by DFT methodology with the B3LYP hybrid functional, which has proven to be a reliable method for hydrogen-bonding description.<sup>41–44</sup> The complexes selected for the present work had large interaction energies, and thus, the DFT methodology was appropriate. However, MP2 calculations were also done to test the results. A 6-311+G(3df,2p) basis set of adequate quality was chosen, as indicated by the small BSSE found for the complexes.

As listed in Table III, the binding energies had high values, and, given that two hydrogen bonds were present for **1–3**, the binding energies resulted in a range of  $\sim -19$  to  $-9$  kcal/mol per hydrogen bond, for **1–3**, respectively. These values were compatible with medium to strong hydrogen bonds. The strength of the hydrogen bonds decreased as the ionic radii of the  $\text{X}^-$  moiety increased.

Complexes **4** and **5** showed binding energies of the same order of magnitude ( $\sim -17$  and  $-12$  kcal/mol per  $\text{X}\cdots\text{O}$  interaction, respectively). Also, for these complexes the binding energy decreased as the metal-cation size increased.

The B3LYP and MP2 binding energies closely matched each other, with differences between them consistently less than 1 kcal/mol, for all the HPX complexes.

As binding-energy studies are affected by the so-called BSSE, the corresponding energy for this error must be corrected, especially for electron-correlation methods. In this work, the BSSE was estimated by the CP method, for all the stationary points on the uncorrected PES. The values are listed in Table III and, as expected from the quality of the basis set, the resulting values were small. DFT gave smaller values than did the MP2 method for the BSSE, and their values ranged between 1.26–0.27 kcal/mol and 2.63–1.53 kcal/mol, respectively.

It should be borne in mind that the BSSE correction to the interaction energies should be performed at the BSSE-counterpoise corrected equilibrium geometry. To get this geometry, the method proposed by S. Simón, M. Duran, and J. J. Dannenberg<sup>15</sup> has been used for all the complexes **1–5**. The minimum geometries on the counterpoise corrected PES

TABLE III. Binding energies (without,  $\Delta E$ , and with BSSE correction,  $\Delta E^{cp}$ ), BSSE, and dipole moment ( $\mu$ ), for the HPX complexes (see Fig. 1), at the different theoretical levels.

	$\Delta E$ (kcal/mol)		BSSE (kcal/mol) <sup>a</sup>		$\Delta E^{cp}$ (kcal/mol) <sup>a</sup>		$\mu$ (Debye)	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
<b>1</b>	-39.91	-40.40	1.26(1.23)	2.63(2.50)	-38.65(-38.68)	-37.77(-37.86)	1.40	1.42
<b>2</b>	-22.14	-23.99	0.52(0.52)	1.77(1.82)	-21.62(-21.62)	-22.22(-22.11)	1.52	1.44
<b>3</b>	-18.55	-20.68	0.27(0.26)	1.53(1.61)	-18.28(-18.30)	-19.16(-19.01)	0.55	0.63
<b>4</b>	-35.42	-35.43	0.65(0.64)	2.14(2.10)	-34.77(-34.77)	-33.29(-33.13)	3.96	4.08
<b>5</b>	-25.01	-25.75	0.67(0.66)	2.16(2.10)	-24.34(-24.34)	-23.59(-23.79)	3.35	3.42

<sup>a</sup>In parentheses the corresponding values for the BSSE-counterpoise corrected PES.

TABLE IV. Harmonic vibrational frequencies<sup>a</sup> (cm<sup>-1</sup>) and zero-point vibrational energies ZPVE (kcal/mol) for the HPX complexes **1–5** and HP monomer, at the MP2(full)/6-311+G(3df,2p) level.

No.	Symm.	<b>1</b>	<b>2</b>	<b>3</b>	Descript.	Symm.	HP	Descript.
$\omega_1$	<b>a</b> <sub>1</sub>	3262(3293)	3460(3478)	3490(3517)	$\nu_s(\text{OH})$	<b>a</b>	3827	$\nu_s(\text{OH})$
$\omega_2$		1702(1682)	1560(1515)	1533(1521)	$\delta_s(\text{OOH})$		1448	$\delta_s(\text{OOH})$
$\omega_3$		895(901)	918(916)	921(923)	$\nu(\text{OO})$		940	$\nu(\text{OO})$
$\omega_4$		372(352)	226(207)	178(161)	$\nu(\text{X}\cdots\text{OO})$		406	$\gamma(\text{HOOH})$
$\omega_5$	<b>a</b> <sub>2</sub>	665(650)	369(298)	267(231)	$\gamma(\text{HOOH})$	<b>b</b>	3827	$\nu_a(\text{OH})$
$\omega_6$	<b>b</b> <sub>1</sub>	957(943)	716(684)	659(646)	$\gamma(\text{out of plane})$		1345	$\delta_a(\text{OOH})$
$\omega_7$	<b>b</b> <sub>2</sub>	3101(3145)	3394(3413)	3436(3466)	$\nu_a(\text{OH})$			
$\omega_8$		1503(1506)	1523(1498)	1520(1517)	$\delta_a(\text{OOH})$			
$\omega_9$		146(120)	191(155)	185(163)	$\nu_a(\text{X}\cdots\text{O})$			
ZPVE		18.0(18.0)	17.7(17.4)	17.4(17.4)				
No.	Symm.	<b>4</b>	<b>5</b>					
$\omega_1$	<b>a</b>	3753(3756)	3772(3774)		$\nu_s(\text{OH})$			
$\omega_2$		1396(1396)	1400(1400)		$\delta_s(\text{OOH})$			
$\omega_3$		925(928)	933(935)		$\nu(\text{OO})$			
$\omega_4$		590(588)	560(559)		$\gamma(\text{HOOH})$			
$\omega_5$		476(451)	257(240)		$\nu(\text{X}\cdots\text{OO})$			
$\omega_6$	<b>b</b>	3746(3748)	3766(3768)		$\nu_a(\text{OH})$			
$\omega_7$		1341(1344)	1368(1371)		$\delta_a(\text{OOH})$			
$\omega_8$		416(407)	338(332)		$\alpha_a(\text{out of plane})$			
$\omega_9$		262(240)	180(163)		$\nu_a(\text{X}\cdots\text{O})$			
ZPVE		18.5(18.4)	18.0(17.9)					

<sup>a</sup>In parentheses the corresponding values for the BSSE-counterpoise corrected PES.

were summarized in Table I, at both levels, while the corresponding binding energies and BSSE on the counterpoise corrected PES were listed in Table III.

As shown in Table I the BSSE-counterpoise corrected minima were almost the same as the uncorrected ones. The main differences came from the  $\text{X}^-\cdots\text{H}$  and  $\text{X}^+\cdots\text{O}$  distances, but these were invariably small in magnitude. In accordance with previous calculations in hydrogen-bonded systems,<sup>31</sup> the effect of CP-correction on the intramolecular parameters was unappreciable. A maximum deviation of 0.002 Å and 0.6 degrees in complex **1** at MP2 level were observed. As expected, the CP-corrected distances  $\text{X}^-\cdots\text{H}$  and  $\text{X}^-\cdots\text{O}$  (intermolecular distances) are systematically longer than the uncorrected ones. Differences at the MP2 level ranged from 0.020 to 0.048 Å, for system **4** and **3**, respectively, while less than 0.01 Å at B3LYP level. The angular features of the complexes were not altered by the BSSE. Due to the cyclic nature of the complexes, the only effect in the intermolecular angular parameters were associated with the enlargement of the intermolecular distance (provided that the intramolecular distances and bond angles remained unchanged).

The BSSE-correction to the interaction energy is not strongly geometry-dependent for these complexes, providing that such a large basis set is used. Even at the MP2 level, the difference between the CP-corrected interaction energy calculated at the uncorrected and CP-corrected geometries are less than 0.2 kcal/mol. These results agree with the good quality of the basis set employed.

### C. Vibrational-frequency analysis

Harmonic vibrational frequencies have been calculated at the MP2/6-311+G(3df,2p) level, for the noncorrected and corrected BSSE PESs. Table IV summarizes the results

for all the complexes together with the HP monomer. According to the Table IV data, **1–5** can be divided in two groups. Complexes **1–3** with hydrogen bonding clearly differed from **4** and **5** with a different interaction nature.

For **1–3**, the harmonic vibrational frequencies  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ ,  $\omega_5$ ,  $\omega_7$ , and  $\omega_8$  corresponded clearly to the HP monomer vibrational modes. Moreover,  $\omega_4$ ,  $\omega_6$ , and  $\omega_9$  were assigned as the intermolecular modes (see Table IV). The  $\omega_4$  mode was associated with the vibration of the  $\text{X}^-$  moiety along the  $\text{C}_2$  axis, and  $\omega_6$  corresponded to the out-of-plane movement of the two hydrogen connecting two possible envelope conformations of the five-membered ring. The  $\omega_9$  mode matched an out-of-the- $\text{C}_2$ -axis movement of the  $\text{X}^-$  in the molecular plane.

Complexes **1–3** also presented a remarkable red shift for the corresponding  $\nu_s(\text{OH})$  and  $\nu_a(\text{OH})$  stretchings ( $\omega_1$  and  $\omega_7$ , respectively). This red shift increased with the strength of the hydrogen bonds involved. The shift values for the  $\omega_1$  were 565, 367, and 337 cm<sup>-1</sup>, and for the  $\omega_7$  were 726, 333, and 391 cm<sup>-1</sup>, for **1–3**, respectively. Red shifts were also observed for the  $\omega_3$  O–O stretching mode. However, the bending modes  $\omega_2$  and  $\omega_8$  underwent a large blue shift.

The above-mentioned shifts were of small magnitude on the BSSE-counterpoise corrected PESs. For **1–3**, major differences were found in the intermolecular modes (except a decreasing of ~20% in  $\omega_5$  for **2**). Frequencies associated with modes  $\omega_9$  and  $\omega_4$  decreased in ~20% and 10%, respectively. Therefore, the frequencies associated to OH stretching modes ( $\omega_1$  and  $\omega_7$ ) slightly increased.

Complexes **4** and **5** showed the interaction between  $\text{X}^+$  and both oxygens. The HP geometry remained similar to the monomer, and therefore, the  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ ,  $\omega_4$ ,  $\omega_6$ , and  $\omega_7$  modes for the HP moiety were less affected. Only the  $\omega_4$  mode [ $\gamma(\text{HOOH})$ ] presented a moderate blue-shift, compat-

ible with a hindered torsion. The intermolecular mode  $\omega_5$  was analogous to the  $\omega_4$  of the 1–3 complexes. Finally, the  $\omega_8$  was described as an asymmetric intermolecular  $\angle X \cdots O-H$  bending, and  $\omega_9$  was similar to the corresponding  $\omega_9$  of the 1–3 complexes.

The 4 and 5 BSSE-counterpoise corrected PES frequencies were very similar to the noncorrected ones except for the intermolecular modes, highlighting the importance of obtaining the counterpoise-corrected frequencies despite the highly similar geometries obtained.

## V. CONCLUSION

Five new HP complexes have been characterized at the B3LYP/6-311+G(3df,2p) and MP2(full)/6-311+G(3df,2p). The levels and basis set used were adequate, given the small BSSE obtained. The computed binding energies of the complexes yielded medium to strong hydrogen-bond interactions for 1–3 and strong electrostatic interactions for 4 and 5. The results obtained at both levels were highly similar, showing that the DFT B3LYP model is a good choice for medium intermolecular interactions. The BSSE-counterpoise corrected PES geometry minima were calculated, giving values very similar to the uncorrected ones. These results were compatible with the small BSSE errors found. The application of the counterpoise corrected PES method has shown its utility in describing the intermolecular vibrational modes, and will be particularly useful for systems where the BSSE is difficult to reduce (large systems and medium basis sets with correlated methods).

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Supporting Information Available: Table SI-I containing the Total Energies for all the minimum complexes and monomers on the BSSE noncorrected and corrected PESs (1 page). Ordering information is given on any current masthead page.

- <sup>1</sup>R. P. Wayne, *Chemistry of Atmospheres* (Clarendon, Oxford, 1991).
- <sup>2</sup>G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Kluwer Academic, Oxford, 1993).
- <sup>3</sup>M. S. Cooper, H. Heaney, A. J. Newbold, and W. R. Sanderson, *Synlett* **1990**, 533.
- <sup>4</sup>K. B. Beckman and B. N. Ames, *Physiol. Rev.* **78**, 547 (1998).
- <sup>5</sup>J. A. Dobado and J. Molina, *J. Phys. Chem.* **97**, 7499 (1993).
- <sup>6</sup>O. Mo, M. Yañez, I. Rozas, and J. Elguero, *J. Chem. Phys.* **100**, 2871 (1994).
- <sup>7</sup>L. Gonzalez, O. Mo, and M. Yañez, *J. Comput. Chem.* **18**, 1124 (1997).
- <sup>8</sup>J. A. Dobado and J. Molina, *J. Phys. Chem.* **98**, 1819 (1994).
- <sup>9</sup>O. Mo, M. Yañez, I. Rozas, and J. Elguero, *Chem. Phys. Lett.* **219**, 45 (1994).
- <sup>10</sup>J. A. Dobado and J. Molina, *J. Phys. Chem.* **98**, 7819 (1994).
- <sup>11</sup>J. A. Dobado, J. Molina, and D. Portal, *J. Phys. Chem. A* **102**, 778 (1998).
- <sup>12</sup>H. B. Jansen and P. Ross, *Chem. Phys. Lett.* **3**, 140 (1969).
- <sup>13</sup>S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).

- <sup>14</sup>S. S. Xantheas, *J. Chem. Phys.* **104**, 8821 (1996).
- <sup>15</sup>S. Simón, M. Duran, and J. J. Dannenberg, *J. Chem. Phys.* **105**, 11024 (1996).
- <sup>16</sup>P. Hobzsa, B. Paizs, O. Bludský, M. Duran, J. J. Dannenberg, and S. Suhai, *J. Chem. Phys.* (submitted).
- <sup>17</sup>K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **102**, 2032 (1995).
- <sup>18</sup>T. van Mouric, A. K. Wilson, A. K. Peterson, D. E. Woon, and T. H. Dunning, Jr., *Adv. Quantum Chem.* **31**, 105 (1998).
- <sup>19</sup>P. Salvador and M. Duran, *J. Chem. Phys.* (submitted).
- <sup>20</sup>A. D. Sadlej, *J. Chem. Phys.* **95**, 6705 (1991).
- <sup>21</sup>I. Mayer, *Int. J. Quantum Chem.* **23**, 341 (1983).
- <sup>22</sup>I. Mayer and Á. Vibók, *Chem. Phys. Lett.* **140**, 558 (1987).
- <sup>23</sup>I. Mayer, P. R. Surján, and Á. Vibók, *Int. J. Quantum Chem.* **36**, 225 (1989).
- <sup>24</sup>I. Mayer, Á. Vibók, and P. Valiron, *Chem. Phys. Lett.* **224**, 166 (1994).
- <sup>25</sup>I. Mayer, P. R. Surján, and Á. Vibók, *Int. J. Quantum Chem., Symp.* **23**, 281 (1989).
- <sup>26</sup>M. Kieninger, S. Suhai, and I. Mayer, *Chem. Phys. Lett.* **230**, 485 (1994).
- <sup>27</sup>E. Gianinetti, M. Raimondi, and E. Tornaghi, *Int. J. Quantum Chem.* **60**, 157 (1996).
- <sup>28</sup>F. F. Muguet and G. W. Robinson, *J. Chem. Phys.* **102**, 3648 (1995).
- <sup>29</sup>D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* **82**, 2418 (1985); **84**, 4113 (1986); **86**, 3760 (1987).
- <sup>30</sup>M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.* **84**, 2279 (1986).
- <sup>31</sup>B. Paizs, S. Salvador, M. Duran, and S. Suhai, *J. Comput. Chem.* (accepted).
- <sup>32</sup>J. J. Novoa, M. Planas, and M. C. Rovira, *Chem. Phys. Lett.* **251**, 33 (1996).
- <sup>33</sup>J. Gao, D. S. Garner, and W. L. Jorgensen, *J. Am. Chem. Soc.* **108**, 4784 (1986).
- <sup>34</sup>E. V. Stefanovich and T. N. Truong, *J. Chem. Phys.* **104**, 2946 (1996).
- <sup>35</sup>R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- <sup>36</sup>R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1990).
- <sup>37</sup>E. S. Kryachko and E. V. Ludeña, *Energy Density Functional Theory of Many Electron Systems* (Kluwer Academic, London, 1990).
- <sup>38</sup>J. Labanowski, Ed. *Density Functional Methods in Chemistry*, edited by J. Labanowski (Springer, New York, 1991).
- <sup>39</sup>T. Ziegler, *Chem. Rev.* **91**, 651 (1991).
- <sup>40</sup>J. A. Dobado, J. Molina, and D. Portal, *J. Mol. Struct.: THEOCHEM* **433**, 181 (1998).
- <sup>41</sup>Z. Latajka and Y. Bouteiller, *J. Chem. Phys.* **101**, 9793 (1994).
- <sup>42</sup>J. J. Novoa and C. Sosa, *J. Phys. Chem.* **99**, 15837 (1995).
- <sup>43</sup>A. T. Pudziański, *J. Phys. Chem.* **100**, 4781 (1996).
- <sup>44</sup>D. R. Hamann, *Phys. Rev. B* **55**, 10157 (1997).
- <sup>45</sup>G. Lendvay and I. Mayer, *Chem. Phys. Lett.* **297**, 365 (1998).
- <sup>46</sup>GAUSSIAN 94, revision C.2., M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. Foresman, B. B. Cioslowski, A. Stefanov, M. Nanayakkara, J. B. Challacombe, C. Y. Peng, P. V. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.
- <sup>47</sup>GAUSSIAN 98, Revision A.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian Inc. Pittsburgh, PA, 1998.
- <sup>48</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>49</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

- <sup>50</sup>P. Pulay, *J. Comput. Chem.* **3**, 556 (1982).
- <sup>51</sup>R. Fletcher, *Practical Methods of Optimization Vol. 1* (Wiley, New York, 1980).
- <sup>52</sup>F. W. Biegler-König, R. F. W. Bader, and T. H. Tang, *J. Comput. Chem.* **3**, 317 (1982).
- <sup>53</sup>R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Clarendon, Oxford, 1990).
- <sup>54</sup>R. F. W. Bader, *Chem. Rev.* **91**, 893 (1991).
- <sup>55</sup>J. A. Dobado, J. Molina, H. Martínez-García, and M. R. Sundberg, *J. Am. Chem. Soc.* **120**, 8461 (1998).
- <sup>56</sup>R. F. W. Bader in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer (Wiley, Chichester, 1998).
- <sup>57</sup>P. L. A. Popelier, *Comput. Phys. Commun.* **93**, 212 (1996).
- <sup>58</sup>For example, the global minimum in the HP $\cdots$ urea complex have two hydrogen bonds with  $\rho(r)$  values of 0.036 and  $0.024e/a_0^3$ , and  $\Delta E^{CP} = -10.29$  kcal/mol.