A chemometrical study of intermolecular properties of hydrogen-bonded complexes formed by $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ with X = F, CN, NC, and CCH

**Boaz G. Oliveira · Regiane C. M. U. Araújo ·
Antônio B. Carvalho · Mozart N. Ramos**

Abstract We presents a chemometrical study of the intermolecular properties of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes with X = F, CN, NC, and CCH. Through the MP2 perturbation theory and B3LYP hybrid functional, as well as modifications on 6-31ijGk basis sets with i = triple-zeta, j = diffuse and k = polarization functions, systematic tendencies in the $R_{(n \cdots HX)}$ hydrogen bond distances and $\upsilon_{(n \cdots HX)}$ stretch frequencies were determined by the hierarchical cluster analysis, two level factorial designs and principal component analysis. Based on well-fitted math models, not only because polarization functions provide a great variance on statistical analysis, but this basis set reproduces more efficiently the available experimental results. Moreover, independent of whether the quality on basis set is increased, the effects yielded by both DFT and MP2 were not considered important in the statistical analysis.

Keywords Chemometric techniques ·
Hydrogen-bonded complexes · MP2 · 3LYP

Introduction

The viability to investigate properties of electronic structure with the purpose to interpret and justify their molecular phenomena is, traditionally, one cornerstone of chemistry. In computational chemistry, the correct choice of an adequate *ab initio* basis to study a molecular system still is considered an intriguing point among the theoreticians. Although some works reports that an appropriate basis set can describe traditional phenomena or else propose new insights with plausible perspectives [1–3], there is not a procedure to elect the ideal basis set, what in some cases can lead to an arbitrary choice of this parameter. However, some statistical studies have revealed the remarkable influence of the basis sets and quantum-chemical methods on analysis of molecular properties of several systems [4–10], including those formed by hydrogen bonds [11, 12]. Nevertheless, it is well-known that in comparison with results obtained from HF (Hartree-Fock) [13] calculations, the molecular properties of hydrogen complexes [14] are described more efficiently by means of thesecond-order Møller-Plesset perturbation theory (MP2) [15] method. On the other hand, it has been documented that density functional theory (DFT) [16, 17] is also an efficient method, where its potentiality has been satisfactorily demonstrated in several promulgated studies, as for example in analysis of properties of hydrogen-bonded complexes [18–33]. Although it is well-established that both MP2 and DFT are the most popular methods used to evaluate the electronic correlation effects [34], it has been observed that DFT appears as an alternative computational scheme at the *ab initio* formalism [35] because the efficiency of exchange, correlation and hybrid functionals has been successfully demonstrated, in particular for studies of chemical, physical and biological systems [36–38].

In practice, Hohenberg-Kohn-Sham protocol offers a great advantage in comparison with the *ab initio* methods, one of them is the low computational demand.

B. G. Oliveira (✉) · R. C. M. U. Araújo · A. B. Carvalho
Departamento de Química, Universidade Federal da Paraíba,
58036-300 João Pessoa, PB, Brazil
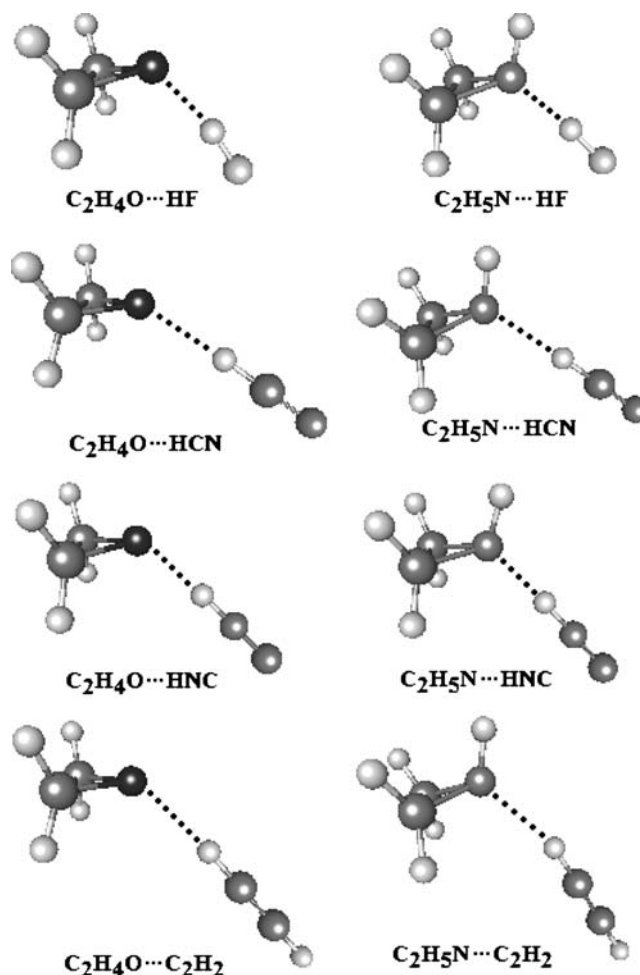e-mail: boazgaldino@gmail.com

M. N. Ramos
Departamento de Química Fundamental,
Universidade Federal de Pernambuco,
50739-901 Recife, PE, Brazil

In studies of molecular properties of hydrogen-bonded complexes [39, 40], for instance, it is vital to consider the effects of electronic correlation, although some theoreticians are still not convinced that DFT is an able method due to its limitation for describing dispersion forces [41]. In spite of this, we are regarding a traditional question related at studies of hydrogen-bonded complexes: what is the most appropriated method for modeling these systems, MP2 or DFT? Or else, the efficiency of these two methods is influenced by any *ab initio* basis sets? So, by taking into account these two highlighted questions, this current study was elaborated with the proposal of comparing the efficiency of MP2 and DFT methods through the analysis of $R_{(n \cdots HX)}$ hydrogen bond distances and $\upsilon_{(n \cdots HX)}$ infrared intermolecular frequencies of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes with X = F, CN, NC, and CCH (see Fig. 1). However, it is essential not only to evaluate which method is the most efficient, but we are admitting the importance of the basis sets and its applicability will be also discussed here. Concomitantly, it is necessary to use a combination of 6-31$ijGk$ split-valence basis set with i = triple-zeta (Tξ); j = diffuse basis set (++), and k = polarization functions (d,p). Thereby, it is generated an immense quantity of results for $R_{(n \cdots HX)}$ and $\upsilon_{(n \cdots HX)}$, which will be treated through the chemometric techniques, such as HCA (Hierarchical Cluster Analysis) [42], TLFD (Two Levels Factorial Design) [43, 44] and PCA (Principal Component Analysis) [45]. As it is well-known that chemometric techniques has been applied successfully in an immensity of situations where questions of chemical, physical and/or biological nature needs to be solved [46], it is necessary to mention that regarding to the main purpose of this work, we thinks that a chemometrical study of intermolecular properties of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes seems to be interesting by one single reason: due the ability of three-membered rings to form intermolecular complexes [47–50] and related systems [51, 52], an indication concerning of what level of theory can be appropriate to examine rings like C_2H_4O and C_2H_5N, in fact this is prerequisite to gain useful information about these systems.

Chemometric techniques

HCA

HCA is a statistical methodology that forms conglomerates patterns through the association among single samples. For the proposal of this work, the HCA similarity S_{ij} of the theoretical methods and basis sets

Fig. 1 Optimized geometries of the $C_2H_4O \cdots HF$, $C_2H_4O \cdots HCN$, $C_2H_4O \cdots HNC$, $C_2H_4O \cdots HCCH$, $C_2H_5N \cdots HF$, $C_2H_5N \cdots HCN$, $C_2H_5N \cdots HNC$, and $C_2H_5N \cdots HCCH$ hydrogen-bonded complexes. In both $R_{(n \cdots HX)}$ and $\upsilon_{(n \cdots HX)}$ terms, n symbolizes the lone electron pairs of the oxygen or nitrogen atoms in the C_2H_4O and C_2H_5N heterocyclics, respectively

will be constructed on the basis of Euclidian criterion according to:

$$S_{ab} = 1 - \frac{d_{ab}}{d_{max}} \qquad (1)$$

where d_{ab} is the distance between a and b samples, as well as the d_{max} is the maximum distance for any connected point. Even though qualitatively, the application of HCA can give us a description of similarity among the theoretical levels used to study the $R_{(n \cdots HX)}$ hydrogen bond distances and $\upsilon_{(n \cdots HX)}$ stretch frequencies of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes.

TLFD

To obtain a chemometrical model formed justly by relevant effects, the TLFD technique performs a complete variation

in theoretical methods with the purpose to quantify the contributions of DFT and MP2, as well as of basis sets. Thus, we admitted the Pople's 6-3$ijGk$ [53] split-valence as our standard basis set and considering both DFT and MP2, the TLFD modifications are treated in four steps summarized below:

(I) i Using triple-zeta (Tξ) instead of double (Dξ) valence functions [54];
(II) j Including or not diffuse functions (++) [55];
(III) k Adding or not polarization functions (d,p) [56];
(IV) l Performing DFT instead of MP2 calculations.

Through these factors, it is built a simplified mathematical model that includes the most relevant effects U_k:

$$U^{EST} = \overline{U}_X + \sum_{m=1}^{n} U_k \qquad (2)$$

In Eq. (2) U^{EST} and $\overline{U}_X$ corresponds to estimated and medium values of the intermolecular properties $R_{(n \cdots HX)}$ or $\upsilon_{(n \cdots HX)}$ of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes. Moreover, the k coefficient is a dummy variable, which during the analysis is equal to +1 and −1 when the corresponding factor (i, j, k or l) is present or absent, respectively.

PCA

PCA are vectors obtained from the diagonalization of $\mathbf{X^t X}$ covariance matrix, where $\mathbf{X}$ are the original data represented in a multidimensional space [57, 58]. In the present case, the $\mathbf{X}$ matrix has 16 rows (theoretical levels, see TLFD section) and 4 columns ($C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes with X = F, CN, NC or CCH, see Fig. 1), where the largest eigenvalue of $\mathbf{X^t X}$ is interpreted as statistical information explained by the first principal component ($\Theta 1$), which if possible, describes the maximum variance (MV) governed by Eq. (3).

$$MV = v1.\Theta 1 + e_1 \qquad (3)$$

If the variance result is unsatisfactory, it is request a second principal component ($\Theta 2$), which is computed automatically. This procedure is repeated until to obtain the so desired maximum variance.

$$MV = v1.\Theta 1 + v2.\Theta 2 + e2 \qquad (4)$$

Computational scheme and statistical programs

To optimize the geometries of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes, all theoretical calculations related to the MP2 and DFT methods, as well as the 6-3$ijGk$ basis sets were performed on the GAUSSIAN 98W [59] software. For DFT calculations, it was used the B3LYP hybrid [60], whose formalism is defined by the Becke's three functional parameter [61] combined with the LYP non-local correlation term [62]. The results of the TLFD, HCA and PCA were obtained by the programs FATORIAL 1.0 [63, 64], STATISTICA 5.0 [65] and UNSCRAMBLER 7.5 [66], respectively.

Results

Structural parameter: $R_{(n \cdots HX)}$ hydrogen bond distance

HCA

The Table 1 presents the theoretical values of the $R_{(n \cdots HX)}$ hydrogen bond distances of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes. Initially, the application of HCA provided tendencies in $R_{(n \cdots HX)}$ values, as can be observed in Fig. 2. Named as G_2, this cluster indicates a great similarity among data obtained by the (d,p) polarization functions. However, G_1 and G_3 clusters are also formed and some interesting informations can be extracted from them. Note that, G_1 corresponds basically to (++) diffuse functions, whereas G_3 to smaller basis sets at MP2 level. If B3LYP is concerned, small basis sets without (++) diffuse functions leads to results similar to MP2, so that the results fall in G_1 rather than G_3. This is known and, if we compare with post-HF methods [67], it is well established that B3LYP was implemented with purpose to execute calculations by using moderate size basis sets instead of larger ones.

TLFD

The TLFD results are listed in Table 2. We can observe that (d,p) polarizations and B3LYP functional are the most significant effects, whose contributions yields a systematic increases on $R_{(n \cdots HX)}$ distances in 0.040 Å and 0.093 Å, as well as diminishes in −0.020 Å and -0.026 Å for the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes, respectively. However, even though by increasing $R_{(n \cdots HX)}$ in 0.024 Å and 0.025 Å, the interaction effect [(B3LYP)-(d,p)] provides a significant contribution to the TLFD analysis. Thus, the TLFD models for $R_{(n \cdots HX)}$ hydrogen bond distances of the $C_2H_4O \cdots HX$ and $C_2H_5N \cdots HX$ hydrogen-bonded complexes are represented by the Eqs. (5) and (6), respectively.

Table 1 Theoretical values of the $R_{(n\cdots HX)}$ hydrogen bond distances of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

Calculations	X			
	F	CN	NC	CCH
MP2/6-31G	1.7200 (1.6222)	1.9932 (1.9579)	1.7800 (1.6970)	2.1416 (2.1017)
MP2/6-311G	1.6861 (1.5787)	1.9817 (1.9434)	1.7435 (1.6568)	2.1528 (2.0937)
MP2/6-31++G	1.6453 (1.5060)	1.9341 (1.9340)	1.7365 (1.6583)	2.0261 (2.0446)
MP2/6-311++G	1.6435 (1.5268)	1.9600 (1.9635)	1.7396 (1.6601)	2.0862 (2.1037)
MP2/6-31G (d,p)	1.7112 (1.6880)	1.9913 (2.0207)	1.7554 (1.7384)	2.1363 (2.1594)
MP2/6-311G (d,p)	1.6998 (1.6844)	1.9849 (2.0029)	1.7242 (1.7124)	2.1344 (2.1391)
MP2/6-31++G (d,p)	1.6572 (1.6106)	2.0082 (2.0248)	1.7476 (1.7101)	2.1322 (2.1345)
MP2/6-311++G (d,p)	1.6712 (1.6520)	2.0191 (2.0203)	1.7366 (1.7067)	2.1452 (2.1376)
B3LYP/6-31G	1.6436 (1.5323)	1.9046 (1.8605)	1.7207 (1.6308)	2.0679 (2.0383)
B3LYP/6-311G	1.6295 (1.5198)	1.9293 (1.9005)	1.7324 (1.6582)	2.0805 (2.0635)
B3LYP/6-31++G	1.5695 (1.4201)	1.9117 (1.8715)	1.7112 (1.6018)	2.0438 (2.0300)
B3LYP/6-311++G	1.5901 (1.4667)	1.9280 (1.9099)	1.7356 (1.6583)	2.0760 (2.0689)
B3LYP/6-31G (d,p)	1.7010 (1.6666)	1.9705 (1.9787)	1.7620 (1.7414)	2.1275 (2.1420)
B3LYP/6-311G (d,p)	1.6868 (1.6560)	1.9906 (2.0112)	1.7652 (1.7512)	2.1311 (2.1641)
B3LYP/6-31++G (d,p)	1.6326 (1.5890)	2.0063 (1.9940)	1.7551 (1.7085)	2.1404 (2.1446)
B3LYP/6-311++G (d,p)	1.6623 (1.6227)	2.0091 (2.0209)	1.7767 (1.7459)	2.1604 (2.1846)

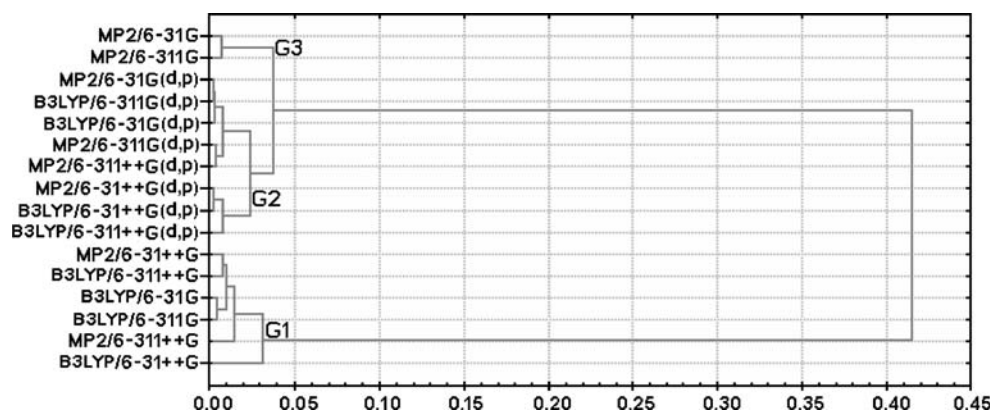*Values of the $C_2H_5N\cdots HX$ hydrogen-bonded complexes are gathered in parenthesis;
*All values are given in Å.

$$R^{EST}_{(n\cdots HX)} = \overline{R}_{X_{(n\cdots HX)}} - 0.0095\Delta(++)$$
$$+ 0.0050\,\Delta[(T\xi) - (++)]$$
$$+ 0.0200\,\Delta(d,p)$$
$$+ 0.0080\,\Delta[(++) - (d,p)]$$
$$- 0.0100\,\Delta(B3LYP)$$
$$+ 0.0055\,\Delta[(B3LYP) - (++)]$$
$$+ 0.0120\,\Delta[(B3LYP) - (d,p)]$$
$$- 0.0078\,\Delta[(B3LYP) - (++) - (d,p)] \quad (5)$$

$$R^{EST}_{(n\cdots HX)} = \overline{R}_{X_{(n\cdots HX)}} - 0.0055\,\Delta(T\xi) - 0.01\,\Delta(++)$$
$$+ 0.0079\,\Delta[(T\xi) - (++)]$$
$$+ 0.0465\,\Delta(d,p) - 0.0131\,\Delta(B3LYP)$$
$$+ 0.0125\,\Delta[(B3LYP) - (d,p)] \quad (6)$$

Note that, some other effects were also included in TLFD, such as $(T\xi)$ valence and $(++)$ diffuse functions. As can be seen in Fig. 3, the R^2 linear correlation square coefficient of 0.99 indicates a good agreement between the $R^{EST}_{(n\cdots HX)}$ estimated results and $\overline{R}_{X_{(n\cdots HX)}}$ medium values of the hydrogen bond distances of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes.

Fig. 2 HCA graph of the $R_{(n\cdots HX)}$ theoretical hydrogen bond distances of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes
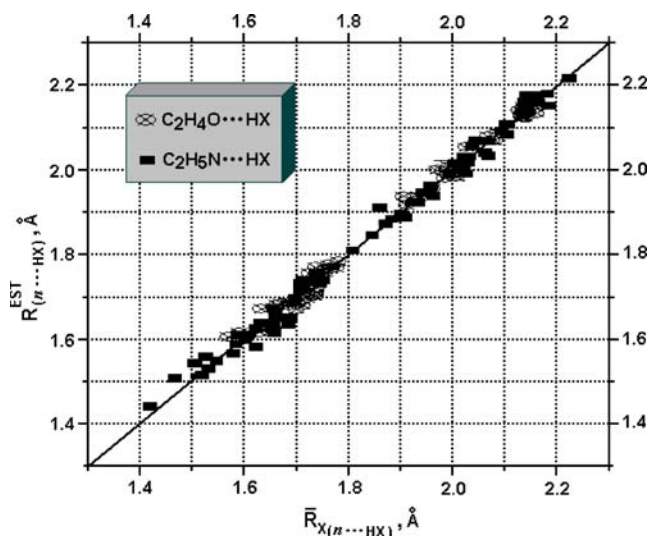
Table 2 Predominant effects of the TLFD analysis of the $R_{(n\cdots HX)}$ hydrogen bond distances of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

Effects	X				$\overline{U}_x$
	F	CN	NC	CCH	
(i)	— (—)	0.0103 (0.016)	— (0.008)	0.018 (0.02)	— (0.011)
(j)	−0.0501 (−0.0692)	— (—)	−0.005 (−0.017)	−0.02 (−0.006)	−0.019 (−0.02)
(i)-(j)	0.0171 (0.0265)	— (0.0062)	0.0113 (0.015)	0.012 (0.015)	0.01 (0.0158)
(k)	0.0368 (0.1242)	0.054 0.0915)	0.0154 (0.074)	0.054 (0.083)	0.04 (0.093)
(j)-(k)	0.007 (0.0143)	0.0225 (—)	0.008 (—)	0.0324 (—)	0.0174 (—)
(l)	−0.04 (−0.0494)	−0.028 (−0.04)	— (−0.0054)	−0.016 (−0.01)	−0.02 (−0.026)
(l)-(j)	— (—)	0.0112 (—)	0.0051 (—)	0.0236 (—)	0.01 (—)
(l)-(k)	0.0257 (0.024)	0.027 (0.024)	0.024 (0.0253)	0.018 (0.026)	0.024 (0.025)
(l)-(j)-(k)	— (—)	−0.0104 (—)	−0.0051 (—)	−0.0475 (—)	−0.0157 (—)

* Values of the $C_2H_5N\cdots HX$ hydrogen-bonded complexes are gathered in parenthesis;

* $i = (T\xi)$ triple-zeta basis sets; $j = (++)$ diffuse functions; $k = (d,p)$ polarization functions and l = B3LYP calculations.

PCA

In terms of PCA, according to Figs. 4 and 5, it can be seen that (d,p) polarizations are described by $\Theta1$ axis, which accounts for 80% and 81% of variance for the $R_{(n\cdots HX)}$ hydrogen bond distance values of the correspondent $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes. It should be also noticeable that, as $\Theta2$ explains 14% and 16% of variance, we would like to emphasize that meaningful effects are also explained by $\Theta2$, for instance the (++) diffuse functions. Indeed, the PCA analysis yielded a satisfactory description of variance if the results of second component are included into the chemometrical analysis. As such, both $\Theta1$ and $\Theta2$ account for 94% and 97% of the total variance.

Fig. 3 Plot of the $R_{(n\cdots HX)}^{EST}$ estimated hydrogen bond distances *versus* the correspondent $R_{(n\cdots HX)}$ theoretical values of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

Not only in terms of (d,p) polarization functions, which appropriately describes the polarizability and strain energies of the C_2H_4O and C_2H_5N heterorings, but the great importance of (++) diffuse functions is related with its capacity of describing chemical systems with larger spatial region and trends of expansion due to their electrons are placed relatively far from the nuclei, i. e., molecules with electron pairs or even anions [68]. For the analysis of the $R_{(n\cdots HX)}$ values, however, these concepts makes reference to n lone electron pairs of oxygen and nitrogen atoms on $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes, respectively. In regards to the acids, the loading Eqs. (7), (8), (9), and (10) demonstrates that hydrofluoric acid is the most important proton donor due to its great contribution for the variance data in both $\Theta1$ and $\Theta2$ axis.
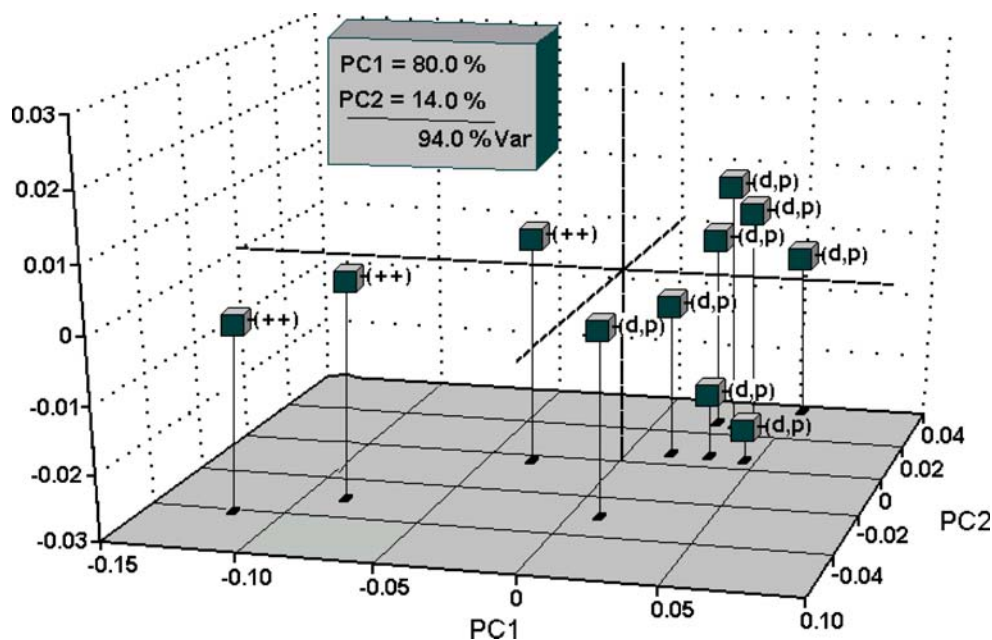
$$\Theta1(C_2H_4O\cdots HX) = 0.60R_{(n\cdots HF)} + 0.53R_{(n\cdots HCN)} + 0.22R_{(n\cdots HNC)} + 0.55R_{(n\cdots HCCH)} \tag{7}$$

$$\Theta1(C_2H_5N\cdots HX) = 0.69R_{(n\cdots HF)} + 0.45R_{(n\cdots HCN)} + 0.37R_{(n\cdots HNC)} + 0.41R_{(n\cdots HCCH)} \tag{8}$$

$$\Theta2(C_2H_4O\cdots HX) = 0.82R_{(n\cdots HF)} - 0.44R_{(n\cdots HCN)} - 0.002R_{(n\cdots HNC)} - 0.36R_{(n\cdots HCCH)} \tag{9}$$

$$\Theta2(C_2H_5N\cdots HX) = 0.70R_{(n\cdots HF)} - 0.56R_{(n\cdots HCN)} - 0.17R_{(n\cdots HNC)} - 0.40R_{(n\cdots HCCH)} \tag{10}$$
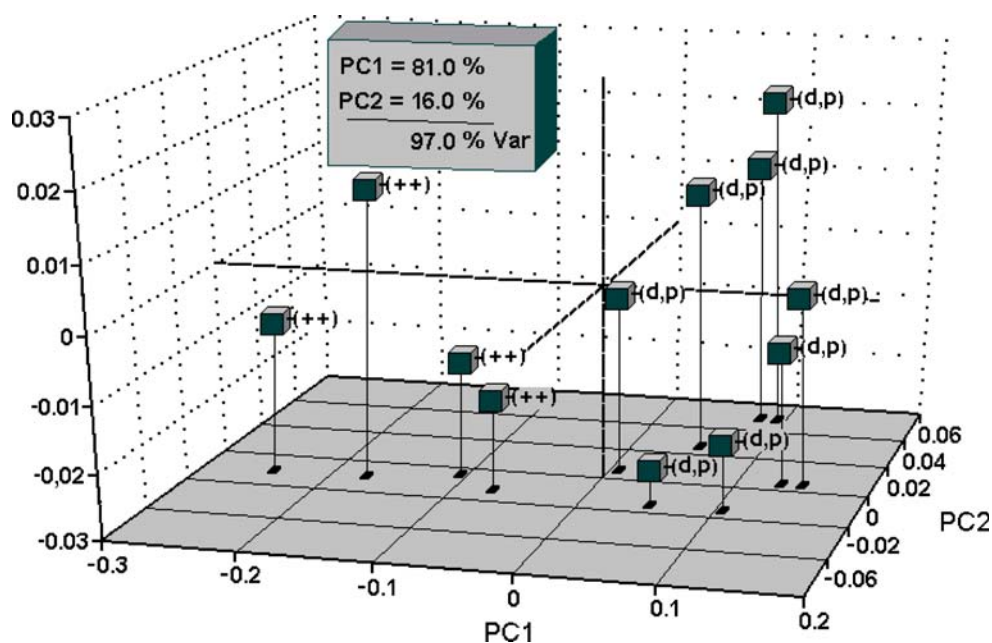
Fig. 4 PCA scores of the $R_{(n \cdots HX)}$ theoretical hydrogen bond distances of the $C_2H_4O \cdots HX$ hydrogen-bonded complexes

However, the validation of the chemometrical model still requires a comparative study with experimental data. Some time ago, the experimental geometries of the $C_2H_4O \cdots HF$ and $C_2H_4O \cdots C_2H_2$ hydrogen-bonded complexes were explained by Legon et al. [69, 70] through Fourier transform microwave spectroscopy (FTMS) [71] analysis. In these occasions, the values of 1.70 Å and 2.40 Å for the $R_{(n \cdots HX)}$ hydrogen bond distances of the $C_2H_4O \cdots HF$ and $C_2H_4O \cdots C_2H_2$ complexes were determined. By analyzing the values listed in Table 2, it is clearly perceived that (d,p)

polarizations provide the best concordance of $R_{(n \cdots HX)}$ theoretical hydrogen bond distances in comparison with the FTMS values. For instance, if we make a comparison between MP2/6-31G(d,p) and B3LYP/6-31G(d,p) calculations, which yielded results of 1.7112 Å and 1.7010 Å for $C_2H_4O \cdots HF$, as well as 2.1363 Å and 2.1275 Å for the $C_2H_4O \cdots C_2H_2$ complexes, it must be noted that these theoretical results are in good agreement with the experimental data of 1.70 Å and 2.40 Å presented above. In this sense, it can be noted that MP2 and B3LYP are considered

Fig. 5 PCA scores of the $R_{(n \cdots HX)}$ theoretical hydrogen bond distances of the $C_2H_5N \cdots HX$ hydrogen-bonded complexes

methods of comparable accuracy. As these are the available experimental data [69, 70], it is with the understanding that such direct comparison is the only test of theory.

Vibrational harmonic spectrum: $\upsilon_{(n\cdots HX)}$ hydrogen bond stretch frequencies

HCA

Table 3 presents the theoretical values of the $\upsilon_{(n\cdots HX)}$ hydrogen bond stretch frequencies of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes. Likewise to structural analysis, the same procedure was employed to examine the theoretical values of the hydrogen bonds frequencies, i.e, the HCA, FDTL and PCA techniques were applied in sequence. For HCA evaluation, the tree cluster presented in Fig. 6 characterizes a G_1 group basically formed by (d,p) polarization functions. For remaining factors, neither similarity was observed as very important.

TLFD

Nevertheless, Table 4 lists the TLFD results of the $\upsilon_{(n\cdots HX)}$ hydrogen bonds frequencies of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes. As we can see, the main effects are indicated by (d,p) polarizations and [(B3LYP)-(d,p)] interaction effects, which decreases systematically $\upsilon_{(n\cdots HX)}$ in -8.9 cm^{-1} and -29.3 cm^{-1}, as well as in -5.4 cm^{-1} and -7.2 cm^{-1} for the $C_2H_4O\cdots HX$ and

$C_2H_5N\cdots HX$ hydrogen-bonded complexes, respectively. Rather, these effects and others were used to build two TLFD models represented by Eqs. (11) and (12), where the R^2 linear correlation square coefficient of 0.98 indicates a good concordance between $\upsilon_{(n\cdots HX)}^{EST}$ and $\upsilon_{X_{(n\cdots HX)}}$ values of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes, as can be seen in Fig. 7.

$$
\begin{aligned}
\upsilon_{(n\cdots HX)}^{EST} = {} & \overline{\upsilon}_{X_{(n\cdots HX)}} - 3.0\,\Delta(T-\xi) - 0.7\,\Delta(++) \\
& - 0.7\,\Delta[(T\,\xi)-(++)] - 4.4\,\Delta(d,p) \\
& - 2.0\,\Delta[(++)-(d,p)] - 1.5\,\Delta(B3LYP) \\
& - 1.5\,\Delta[(B3LYP)-(++)] \\
& + 1.7\,\Delta[(B3LYP)-(T\,\xi)-(++)] \\
& - 2.7\,\Delta[(B3LYP)-(d,p)]
\end{aligned}
\tag{11}
$$

$$
\begin{aligned}
\upsilon_{(n\cdots HX)}^{EST} = {} & \overline{\upsilon}_{X_{(n\cdots HX)}} - 1.9\,\Delta(T\xi) - 1.5\,\Delta(++) \\
& - 1.9\,\Delta[(T\xi)-(++)] - 14.6\,\Delta(d,p) \\
& - 1.3\,\Delta[(++)-(d,p)] \\
& - 0.9\Delta 0.9\,\Delta(B3) \\
& - 1.2\,\Delta[(B3LYP)-(++)] \\
& + 0.2\,\Delta[(B3LYP)-(T\xi)-(++)] \\
& - 3.6\,\Delta[(B3LYP)-(d,p)]
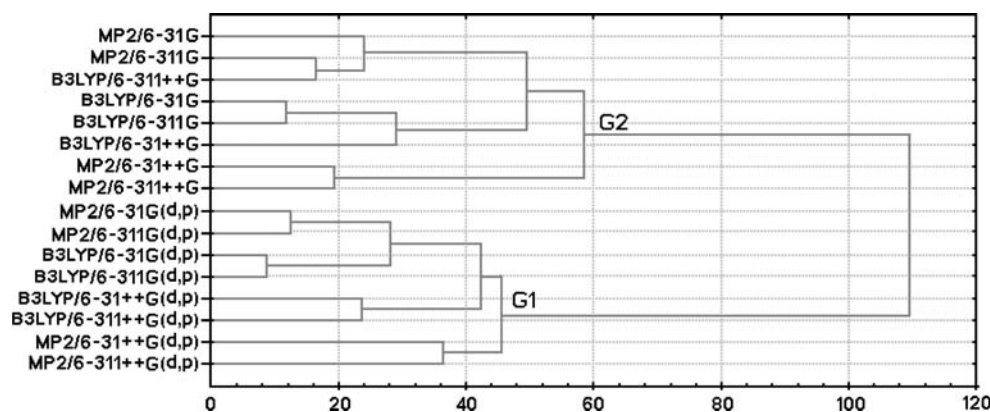\end{aligned}
\tag{12}
$$

Table 3 Theoretical values of the $\upsilon_{(n\cdots HX)}$ hydrogen bond stretch frequencies of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

Calculations	X			
	F	CN	NC	CCH
MP2/6-31G	296.5 (337.5)	160.7 (178.7)	227.8 (267.0)	154.9 (175.7)
MP2/6-311G	301.1 (359.0)	148.6 (173.3)	233.1 (283.8)	147.3 (168.4)
MP2/6-31++G	277.7 (328.5)	159.9 (185.5)	228.7 (274.3)	159.9 (200.5)
MP2/6-311++G	272.8 (334.8)	153.6 (174.2)	221.7 (274.8)	166.0 (181.0)
MP2/6-31G (d,p)	284.2 (305.1)	167.7 (167.5)	236.4 (248.0)	152.0 (164.8)
MP2/6-311G (d,p)	271.7 (301.3)	165.8 (167.1)	236.9 (260.5)	154.5 (170.5)
MP2/6-31++G (d,p)	254.3 (289.5)	145.9 (166.6)	223.1 (249.7)	157.8 (152.6)
MP2/6-311++G (d,p)	252.4 (277.5)	133.8 (160.7)	217.4 (255.1)	121.6 (176.1)
B3LYP/6-31G	323.1 (381.6)	168.9 (186.4)	240.2 (283.2)	159.7 (192.5)
B3LYP/6-311G	321.0 (379.4)	157.3 (179.5)	234.1 (277.6)	148.0 (186.7)
B3LYP/6-31++G	300.3 (387.0)	148.6 (183.0)	224.7 (279.3)	130.8 (200.9)
B3LYP/6-311++G	294.6 (358.6)	153.2 (179.8)	222.4 (270.7)	131.0 (200.2)
B3LYP/6-31G (d,p)	286.8 (320.0)	160.0 (167.8)	227.6 (244.6)	148.3 (169.0)
B3LYP/6-311G (d,p)	282.7 (311.4)	151.3 (162.6)	221.9 (241.3)	140.7 (166.7)
B3LYP/6-31++G (d,p)	262.2 (304.7)	135.4 (161.0)	211.5 (246.6)	119.1 (175.6)
B3LYP/6-311++G (d,p)	254.3 (281.1)	133.8 (157.0)	204.0 (237.5)	112.3 (170.2)

* Values of the $C_2H_5N\cdots HX$ hydrogen-bonded complexes are gathered in parenthesis;
* All values are given in cm^{-1}.

Fig. 6 HCA graph of the theoretical $\upsilon_{(n\cdots HX)}$ stretch frequencies of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

PCA

About PCA, however, the results shows that (d,p) polarization functions and [(B3LYP)-(d,p)] interaction are the most prominent effects, which describes 72% and 80% of variance through the Θ1 axis, as can be seen in Figs. 8 and 9, respectively. Both (d,p) and [(B3LYP)-(d,p)] are placed in left side of Θ1 and Θ2, although the second component contains 24% and 19% of variance for $\upsilon_{(n\cdots HX)}$ values of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes, respectively. Corroborating with the structural analysis, loading Eqs. (13), (14), (15), and (16) says that the hydrofluoric acid has the largest contribution on the variance data.

$$\Theta1(C_2H_4O\cdots HX)= 0.75\upsilon_{(n\cdots HF)}+0.37\upsilon_{(n\cdots HCN)}$$
$$+0.32\upsilon_{(n\cdots HNC)}+0.43\upsilon_{(n\cdots HCCH)}$$
(13)

$$\Theta1(C_2H_5N\cdots HX)= 0.90\upsilon_{(n\cdots HF)}+0.21\upsilon_{(n\cdots HCN)}$$
$$+0.36\upsilon_{(n\cdots HNC)}+0.04\upsilon_{(n\cdots HCCH)}$$
(14)

$$\Theta2(C_2H_4O\cdots HX)= -0.70\upsilon_{(n\cdots HF)}+0.25\upsilon_{(n\cdots HCN)}$$
$$+0.14\upsilon_{(n\cdots HNC)}+0.60\upsilon_{(n\cdots HCCH)}$$
(15)

$$\Theta2(C_2H_5N\cdots HX)= -0.90\upsilon_{(n\cdots HF)}+0.13\upsilon_{(n\cdots HCN)}$$
$$+0.31\upsilon_{(n\cdots HNC)}+0.19\upsilon_{(n\cdots HCCH)}$$
(16)

On the contrary of results found for the hydrogen bond distances, the (d,p) polarizations are identified in the left side of both Θ1 and Θ2 axis. In other words, our model can predict that weaker hydrogen bond frequencies are obtained through the application of (d,p) polarization functions. Comparatively, it was verified that MP2 contributes slightly to the statistical model. It is, in fact, not a surprise because DFT simulates molecular parameters of cyclic hydrogen-bonded complexes very satisfactorily if compared with MP2 [72], or else still more efficiently than HF calculations [73].
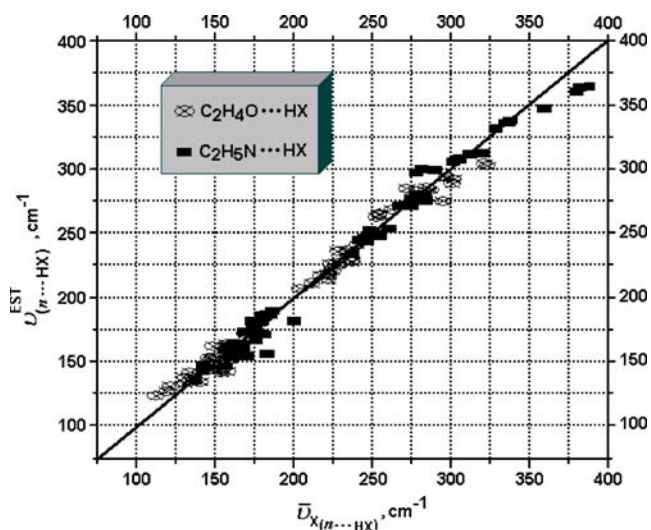
Table 4 Predominant effects of the TLFD analysis of the $\upsilon_{(n\cdots HX)}$ stretch frequencies of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes

Effects	X				$\overline{U}_x$
	F	CN	NC	CCH	
(i)	−2.1 (−6.3)	−6.2 (−5.3)	−3.5 (—)	−12.1 (−4.2)	−6.0 (−3.9)
(j)	−1.2 (−16.7)	−1.4 (−1.9)	−1.3 (−2.2)	−1.7 (8.1)	−1.4 (−3.0)
(i)-(j)	— (−8.0)	2.3 (—)	−2.0 (−4.0)	−6.0 (−3.3)	−1.4 (−3.8)
(k)	−14.8 (−59.5)	−7.1 (−16.2)	−6.7 (−28.4)	−6.8 (−12.9)	−8.9 (−29.3)
(j)-(k)	— (−4.5)	−9.4 (−3.0)	−3.6 (—)	−3.3 (−3.4)	−4.1 (−2.7)
(l)	7.1 (23.8)	−3.4 (—)	−4.8 (−4.0)	−11.0 (−27.2)	−3.0 (−1.8)
(l)-(j)	— (—)	−2.1 (−2.0)	−2.2 (−0.9)	−8.0 (−7.1)	−3.0 (−2.5)
(l)-(i)-(j)	(−2.2) (—)	3.4 (1.9)	2.5 (1.8)	9.6 (—)	3.5 (0.4)
(l)-(k)	−4.2 (−12.9)	−4.4 (−3.8)	−7.3 (−6.8)	−5.3 (−5.1)	−5.4 (−7.2)
(l)-(i)-(k)	— (—)	— (−1.2)	— (—)	(−3.5) (—)	— (—)

*Values of the $C_2H_5N\cdots HX$ hydrogen-bonded complexes are gathered in parenthesis;
*i = (Tξ) triple-zeta basis sets; j = (++) diffuse functions; k = (d,p) polarization functions and l = B3LYP calculations.
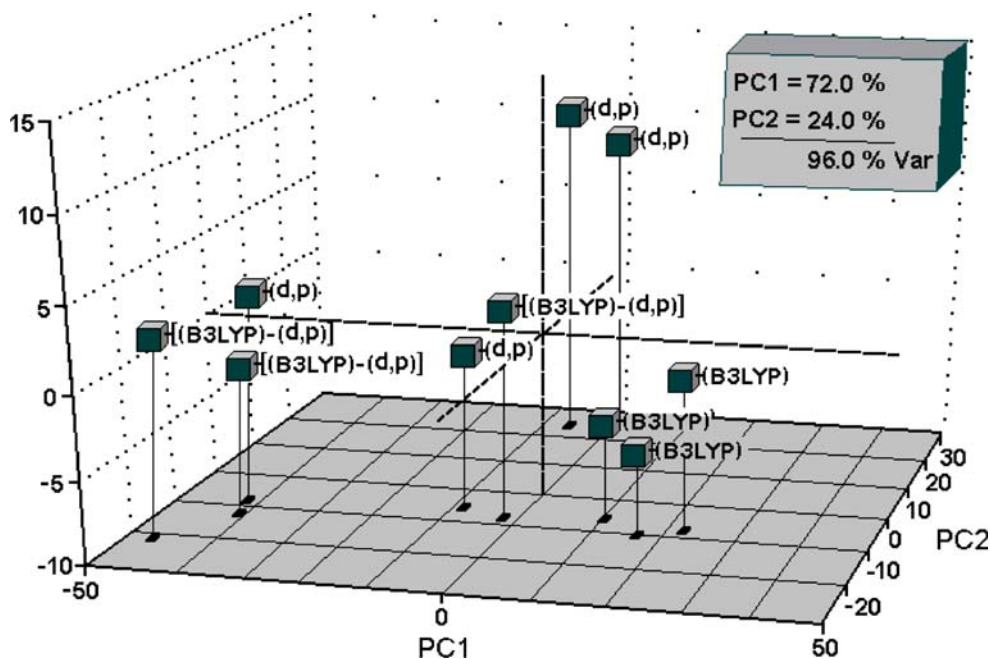
Fig. 7 Plot of the $\upsilon^{EST}_{(n\cdots HX)}$ estimated hydrogen bond stretch frequencies *versus* the correspondent $\upsilon_{(n\cdots HX)}$ theoretical values of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes
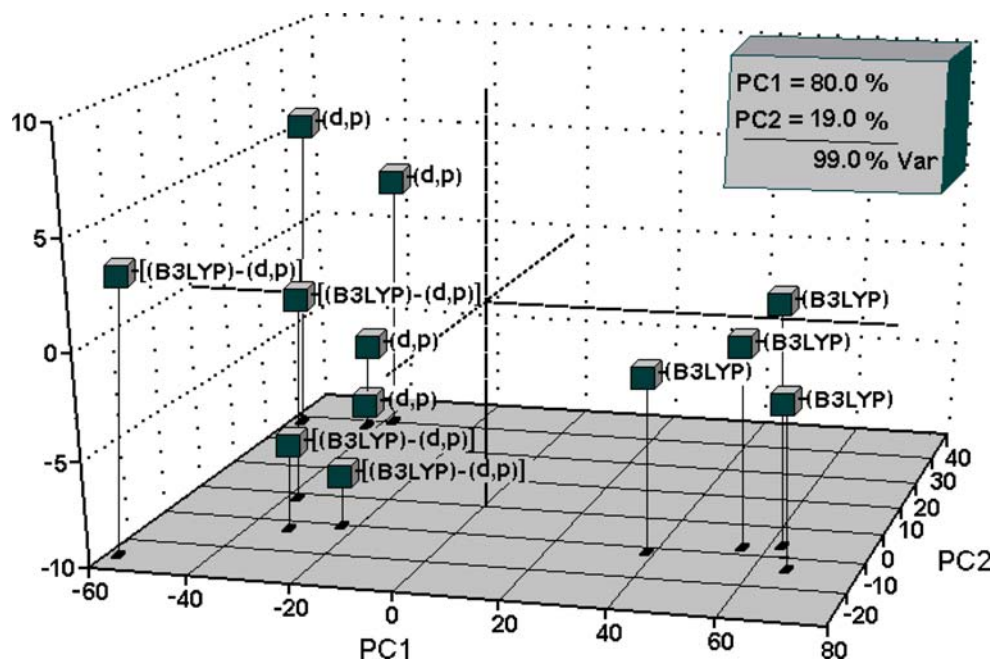
Discussion and perspectives

It is a tradition in our research group to use DFT calculations in studies of hydrogen-bonded complexes [74, 75] and related systems [76]. As reviewed on a number of occasions, it is widely known the efficiency of the B3LYP hybrid functional for describing intermolecular interactions [77–80] but independent of that, it is well to bear in mind that MP2 is considered an unquestionable approach, wherein it was also used in some investigations developed by our research group [14, 81]. So, we have no desire to opine or to enter a discussion if DFT is better than

MP2 and vice-versa, actually we just want to discern the efficiency of these two methods for describing the intermolecular properties of the $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes. Some time ago, we published some works wherein structural, electronic, and vibrational parameters of these complexes were debated. In these works, of course that the B3LYP was admitted but, it used the 6-311 +G(d,p) basis sets to effectuate the calculations, by which is a complete set because there is valence (Tξ) and diffuse (++) functions within its formulation. If we considered the results of our chemometrical analysis, by which it was concluded that (d, p) functions is the most important parameter, it was redundant to include (Tξ) and (++) into our works cited above? [72, 82]. In parts, actually, but on the other hand there is the problem of base sets superposition error (BSSE) [83], wherein if small basis are used, such as 6-31G(d,p), surely that BSSE amounts will be overestimated [84], e.g., the dispersion effects caused by moderate basis sets leads to a correction error on the interaction energy of 8.26–1.55 kJ mol⁻¹, as recently reported by Šponer and Hobza [85]. It is by this statement that, at this moment we are developing a study wherein it is evaluated the dependence of BSSE with the same *ab initio* basis sets used in this work, properly not just related to the $C_2H_4O\cdots HX$ or $C_2H_5N\cdots HX$ systems but, we are extending this study to other hydrogen-bonded complexes with significant differences of intermolecular strength, such as those formed by π and pseudo-π interactions [25, 83–94]. So, as soon as possible, we expect to obtain a measure of how the basis sets can contribute for BSSE calculations. It comes to what is the most important is that the relationship between BSSE and basis sets is well

Fig. 8 PCA scores of the $\upsilon_{(n\cdots HX)}$ theoretical stretch frequencies of the $C_2H_4O\cdots HX$ hydrogen-bonded complexes

Fig. 9 PCA scores of the $\upsilon_{(n\cdots HX)}$ theoretical stretch frequencies of the $C_2H_5N\cdots HX$ hydrogen-bonded complexes

understood but, in a similar way at procedure performed here where DFT and MP2 methods were used, it is worth stressing that this perspective above presented can reveal interesting results, although there are some affirmations about a possible relationship between both DFT and MP2 with accurate BSSE results [95, 96].

Conclusions

The HCA, TLFD and PCA chemometric techniques were used to evaluate the effects of basis sets and quantum-chemical methods on structural parameters and infrared harmonic spectrum of $C_2H_4O\cdots HX$ and $C_2H_5N\cdots HX$ hydrogen-bonded complexes. These three statistical methods were applied with the purpose to ensure that an appropriate level of theory can be elected to describe a property of interest, in such case, the intermolecular distance and its stretch frequency of the complexes mentioned above. In general, the results of our study show that the polarization functions are the most important effect, although other factors were also considered significant, for instance diffuse functions on the analysis of the hydrogen bonds distance. At the interpretation of the hydrogen bonds frequencies, polarization functions and B3LYP functional contributes equally for the statistical analysis upon removal of the other effects. In comparison with HCN, HNC, and HCCH, the PCA results demonstrated that the hydrofluoric acid is the most important variable. Finally, a decisive point is related to the quality of theoretical method, DFT or MP2. In this sense, it was verified that MP2 results alters insignificantly the statistical analysis. Finally we comment

the relation of our current results with theoretical works documented recently [11, 12], where it was known that MP2 always furnished the major contribution to the chemometrical analysis. By taking into account our results debated in this work, DFT seems to be a suitable and efficient approach to study intermolecular properties of hydrogen-bonded complexes [97–100]. Thereby, we would like to emphasize the importance of DFT as a useful method for studying electronic structures and in this sense, only two reasons deserve to be considered: *i*) the lower computational effort and, *ii*) satisfactory reproduction of the available experimental data.

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