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Density functional study of hydrogen-bonded systems: Energetic and vibrational features of some gas-phase adducts of hydrogen fluoride

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Abstract

A series of detailed density functional calculations on hydrogen-bonded gas-phase adducts of the FH molecule for which both experiments and calculations based on traditional approaches were available have been carried out. The adducts were: $(\text{FH})_2$, FH/CO and FH/NH_3 . The adopted methods were: SCF, MP2, S-VWN, B-LYP, B-P86 and B3-LYP. Basis sets were: 6-31G(d,p), 6-31+G(d,p), 6-311++G(d,p), 6-311+G(2d,2p), 6-311+G(3df,2pd), DZ(d,p), cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ. Computed properties were: geometries, harmonic vibrations, binding energies and intensity of the F–H stretching mode of the donor. A detailed analysis of the anharmonicity associated with the F–H stretching mode was also carried out by numerically solving the nuclear Schrödinger equation associated with the F–H mode for both the FH/NH_3 and FH/CO cases. Comparison with previous studies as well as with available experimental data shows that heats of formation computed with the gradient corrected DF methods are as accurate as MP2 or better, when a basis set of at least triple-zeta valence quality with a double set of polarization functions is chosen. All functionals are able to give the correct order of stability for the FH/CO adduct, i.e. the carbon-bound structure as the more stable one, in agreement with MP2 studies. The Pople basis set 6-311+G(2d,2p) appears as good as the correlation-consistent basis set proposed by Dunning, namely aug-cc-pVDZ. Some care should be taken when adopting the 6-31G(d,p) basis set, as for instance in the case of $(\text{FH})_2$ where spurious interactions stabilize cyclic structures with respect to open ones. All DF methods overestimate the shifts in the F–H stretching mode due to the hydrogen-bond interaction, calculated at the harmonic level, and no improvement is brought about by anharmonicity. The increase in the infrared intensity of the FH donor molecule is correctly accounted for. DF methods based on local electron density overestimate both the binding energies and the shifts in the F–H stretching mode showing their unreliability for studying hydrogen-bonding interactions. © 1997 Elsevier Science B.V.

1. Purpose

The hydrogen bond occurs ubiquitously in chemistry: the best characterized systems are however weakly bound, gas-phase species, for which techniques like microwave resonance spectroscopy provide a wide

range of energetic, structural and vibrational data [1]. On the other hand, these systems are simple enough to be tackled computationally, and indeed a large number of ab-initio methods have been applied to the study of H-bound adducts like the hydrogen fluoride dimer [2]. In these cases, computational results and observed geometries are usually assumed to indicate that binding is basically dictated by

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electrostatics [3], although different points of view are available [4]. So far, the vast majority of the computational work carried out in the field of H-bonding concerns SCF and traditional post-SCF techniques, like MP2, CI or CC. However, recent literature has reported the outburst of density functional methods, based on solving the Kohn–Sham equations by means of properly chosen electron density functionals. In the vast majority of cases results obtained by means of the gradient-corrected functionals have the same quality as those usually associated with post-SCF methods like the CCSD(T) method, at a fraction of the computational cost. However, for the case of intermolecular interactions, very few studies have been published. As

for the H-bond, several papers [5–15] have become available in recent years, indicating that gradient-corrected DF methods are quite efficient in calculating the geometry and energy of the interaction of H-bonded adducts. Results are better than SCF and compare to MP2 and even to QCISD, at small fraction of the computational cost. Note that the present DF methods are not able to deal with dispersive interactions [15,16], which also contribute to H-bonding. In contrast, vibrational features of H-bonded complexes (namely, frequency shifts and changes either in the intensity or the anharmonicity of the motions) have been less well studied, in line with the general fact that vibrational features, even with isolated

Table 1
Previous DFT calculations on hydrogen bonded systems

Ref.	System, DF method and basis sets
[5]	(H ₂ O) ₂ , glyoxylic/CHOCHCHOH, NH ₂ CHO/H ₂ O PW86-P86, B-P86, VWN (5211/411/1) N, O, C; (41/1) H
[6]	(H ₂ O) ₂ , (FH) ₂ , (NH ₃) ₂ , C ₂ H ₂ /H ₂ O, CH ₄ /H ₂ O S-null, B-null, X _α , S-VWN, B-VWN, S-LYP, B-LYP, B3-LYP cc-pVDZ, 6-31++G(2d,2p), aug-cc-pVDZ
[7]	(H ₂ O) ₂ , (HCOOH) ₂ , (CH ₃ COOH) ₂ , (CF ₃ COOH) ₂ , (CH ₃ OH) ₂ , (CH ₃ CH ₂ OH) ₂ B-P86 DZVP2, DZVPD, TZVP, TZVPD
[8]	Li ⁺ /OH ₂ , F ⁻ /OH ₂ , (C ₆ H ₆) ₂ , (C ₂ H ₄) ₂ , (Ne) ₂ , (Ar) ₂ C ₆ H ₆ /Ne, C ₆ H ₆ /Ar, (H ₂ O) ₂ , (HF) ₂ , (HCl) ₂ B-LYP, B3-LYP, B3-P86 6-31G(d), 6-31G(d,p), 6-31++G(d,p), 6-311G(d), D95(d,p), D95(2d,2p)
[9]	NH ₃ /NH ₄ ⁺ , (H ₂ O) ₂ , (CH ₃ OH) ₂ B-P86, VWN, PW86-P86 (6311/31/1) N, C, O; (311/1) H; (7111/411/1) N, C, O; (41/1) H (631/31/1) N, C, O; (31/1) H
[10]	(H ₂ S) ₂ , (HCl) ₂ , (HF) ₂ , FH/NH ₃ , (HCN) ₂ , (H ₂ O) ₂ VWN, B-P86, PW86-P86 (7111/411/1) C, N, O, F; (7321/621/1) S, Cl; (41/1) H
[11]	FH/NCCH ₃ , HCl/NCH, HCl/NCCH ₃ , HCl/H ₂ O, (H ₂ O) ₂ , (HF) ₂ , FH/NCH B3-LYP 6-31G(d,p), 6-31+G(d,p)
[12]	(H ₂ O) ₂ B-P86, B3-LYP aug-cc-pVDZ*, aug-cc-pVDZ, aug-cc-pVTZ*, aug-cc-pVTZ aug-cc-pVTZ', aug-cc-pvQZ*, aug-cc-pvQZ'
[13]	(HF) ₂ S-VWN, S-LYP, B-VWN, B-PL, B-LYP, B-P86, B3-LYP, B3-P86, BHandH-LYP 6-311++G(d,p), 6-311++G(2d,2p) 6-311++G(3d,3p), 6-311++G(2df,2pd), 6-311++G(3df,3pd)
[14]	(NH ₃) ₂ S-VWN, B-VWN, B-P86, B-LYP 6-31+G(d,p), 6-31+G(2d,2p), 6-311++G(2df,2pd), (631/31/1) N; (31/1) H

Table 2

Computed and experimental $\Delta H^0(0)$ (kJ/mol) and $\Delta\nu$ (cm^{-1}) for the three adducts. Computed $\Delta\nu$ are at the harmonic level; experimental $\Delta\nu$ are shifts in the fundamental ω_{01} transition. Gas-phase measurements indicated as *gp*. Cold gas matrices measurements labelled with the corresponding atomic symbol

Adduct	Method/basis set	$-\Delta H^0(0)$	$-\Delta\nu$
FH/FH	CCSD(T)/QZ3P ^a	11.63	105
	CCSD(T)/TZ2P+f ^a	12.17	101
	CCSD(T)/TZ2P(f,d) ^a	12.30	107
	Experiment	12.7030.012 ^b	93 (gp) ^c 105 (Ne) ^d 128 (Ar) ^e
FH/NH ₃	MP4/6-311+G(d,p) ^f	42.09	
	QCISD/6-311+G(d,p) ^f	39.62	
	QCISD(T)/6-311+G(d,p) ^f	41.54	
	QCISD(T) ^g	40.0	
	Experiment		912 ^h
FH/CO	MP2/TZ2P ⁱ		165
	MP2/TZ2P ^l	7.68	154
	MP3/6-311++G ^{**} (2d) ^m	6.44	
	MP4/6-31G(d) ^m	10.54	
	QCISD(T)/6-31+G(2d,2p) ⁿ	7.53	
	Experiment	11.81 ^p	117 (gp) ^q 165 (Ar) ^r
FH/OC	MP2/TZ2P ^l	0.12	20
	MP3/6-311++G ^{**} (2d) ^m	3.05	
	MP4/6-31G(d) ^m	4.77	
	QCISD(T)/6-31+G(2d,2p) ⁿ	4.18	
	Experiment		54 (Ar) ^s

^a Ref. [27]. ^b Ref. [28]. ^c Ref. [29]. ^d Ref. [30]. ^e Ref. [31].

^f Ref. [32] geometry and ZPE at MP2/6-31+G(d,p).

^g Ref. [32] geometry and ZPE at MP2/6-31+G(d,p) and corrections at MP2/6-311+G(3df,2p).

^h Ref. [33]. ⁱ Ref. [34]. ^l Ref. [35]. ^m Ref. [36] geometry and ZPE at HF/4-31G.

ⁿ Ref. [37] geometry and ZPE at MP2/6-31+G(d,p). ^r Ref. [38].

^q Ref. [39]. ^s Ref. [41]. ^r Ref. [42].

molecules [17–22], have been paid much less attention than geometry and conformational stability, despite the fact that often the former are more readily measured. We have recently carried out work concerning the interaction of carbon monoxide with alkaline cations [23], and found that DF techniques are very efficient in dealing with systems in which electrostatics dominates, similarly for vibrational features.

In the present paper a series of detailed calculations has been carried out on hydrogen-bonded gas-phase adducts for which both experiments and calculations based on traditional approaches were available. Most popular DF methods recently proposed in the literature were adopted. Both local and gradient-corrected functionals have been used. The results are compared

to those obtained for SCF and MP2 levels. Literature data concerning previous calculations have also been used and reviewed.

The capability of the present DF methods to deal with the vibrational features of H-bonded complexes is also relevant to the study of systems of catalytic interest [24,26].

2. Previous work

Several papers concerning the application of DF methods to the study of H-bonded complexes have been recently published. Table 1 shows the most relevant contributions to the study of intermolecular interactions by means of DF methods which have recently

appeared in the literature. The majority of them concern $(\text{H}_2\text{O})_2$ and $(\text{FH})_2$, and only few also include a detailed frequency analysis. None of the adducts under consideration here were studied at the same theoretical level and for such a large number of basis sets. As far as the authors are aware, no previous frequency calculations at the DFT level have been reported taking anharmonicity into account. Reference [25] includes more details about the computed quantities to be found in previously published papers.

3. Gas phase adducts

Three adducts involving hydrogen fluoride as a proton donor have been considered: (i) with FH itself as H-acceptor (FH/FH); (ii) with ammonia (FH/ NH_3); (iii) with carbon monoxide interacting through either the C (FH/CO) or the O end (FH/OC), respectively (see Fig. 1).

These three cases have been selected because they have already been subjected to extensive calculations adopting traditional computational techniques and/or thoroughly characterized experimentally. Moreover, they span a relatively large range of interaction energies, so that they are representative of H-bonding without proton transfer. The cases of FH/CO and FH/OC are also interesting for ascertaining whether the DF methods may yield the correct order of stability for the two conformers. Table 2 summarizes the data available on the adducts, both computed and measured, which will be used as reference data for the present DF results.

4. Methods of calculation

4.1. Theoretical methods

Traditionally, computational chemistry has been based on the Hartree–Fock method followed by post Hartree–Fock techniques in order to account for electron correlation. The above procedure deals with the computation and refinement of the wave function of the system under study. An alternative approach, known as density functional theory (DFT), was proposed in the early 1930s by Fermi, Dirac and Thomas [43] and further formalized and refined by Hohenberg,

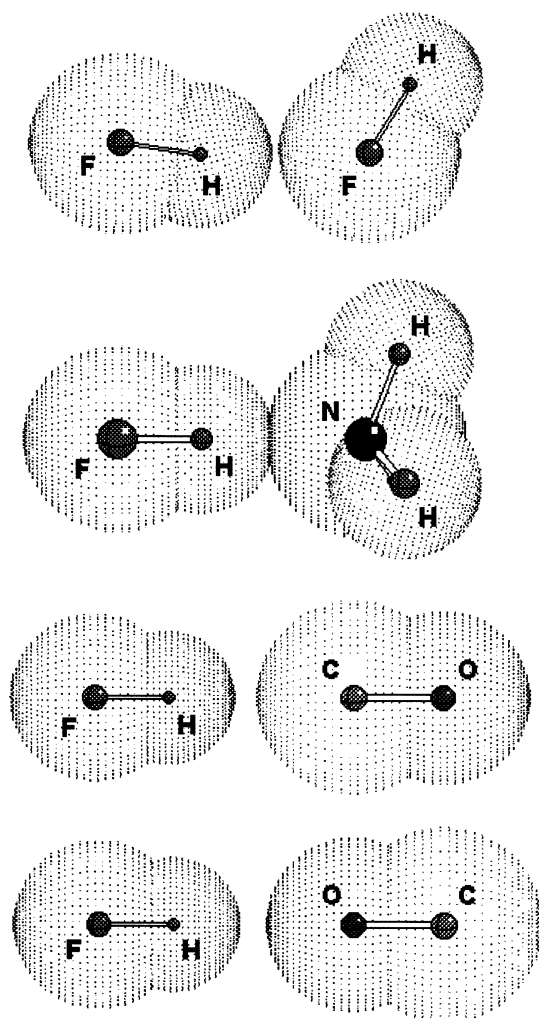


Fig. 1. Structures of the gas-phase adducts. Dots represent the CPK spheres.

Kohn and Sham in the 1960s [44,45]. With DF methods one tries to calculate the electron density function (a function of the 3 spatial coordinates only) instead of the wave function (a function of $3N$ spatial coordinates plus N spin coordinates, in which N is the number of particles of the system). DF methods have been mostly used in the past by solid state physicists but very recently there has been a steadily increasing interest in the computational chemistry community. This is mainly due to a vast improvement in the definition of the exchange-correlation functionals: these functionals are so effective that

even problems which require chemical accuracy can now be tackled. Furthermore, numerically stable integration schemes have also been proposed as well as extensions of the method to deal with traditional gaussian basis sets. Powerful computational chemical codes are now currently available.

All the calculations described in this paper were done using both the Gaussian 92/DFT program [46] and the Gaussian 94 program [47]. The functionals are traditionally separated into exchange and correlation contributions. The exchange functionals used in this work are: (i) S, the Slater exchange functional for the free electron gas, with $\rho(r)^{3/4}$ dependency and theoretical coefficient of 2/3 [48]; (ii) B, Becke's 1988 functional, based on Slater exchange plus corrections including electron density gradient [49]. As far as correlation functionals are concerned, the following proposals have been considered: (i) VWN, the Vosko, Wilk and Nusair 1980 proposal which fits the random phase approximation solution of the uniform electron gas [50]; (ii) LYP, the Lee, Yang and Parr proposal which includes both local and gradient corrected terms [51,52]; (iii) P86, the 1986 gradient-corrected Perdew's proposal based on his 1981 local correlation functional [53]. These functionals were combined to give the following DF methods: S-VWN, B-LYP, B-P86. Additionally we have included in our studies the hybrid method B3, proposed by Becke [54], for the exchange part, combined with the LYP correlation functional to give the B3-LYP method. The B3 component contains a tuned fraction of Hartree–Fock exchange mixed with a pure Becke contribution.

The standard SG-1 grid for the numerical integration [55] has been used for all DFT calculations, which corresponds to the normalgrid option of the Gaussian package. However, for the hydrogen fluoride dimer the finegrid option was used.

4.2. Basis set

Up to ten different basis sets have been used for the present study from both Pople [56], Dunning standard [60–63] and correlation-consistent [57–59] collections, respectively. For the sake of clarity, our results will be reported in the following referring to two different categories of basis sets, namely: (i) polarized basis sets, hereafter referred as POL, including

6-31G(d,p), DZP, cc-pVDZ and cc-pVTZ; (ii) polarized-diffuse basis sets, hereafter referred as POLD, including 6-31+G(d,p), 6-311+G(d,p), 6-311+G(2d,2p), 6-311++G(3df,3pd), aug-cc-pVDZ and aug-cc-pVTZ. In one case (FH/CO) we added diffuse functions, taken from Pople's basis sets, to the DZP basis set to obtain a DZP+ basis set: no relevant differences were however found between DZP+ results and those obtained with the classical 6-31+G(d,p) basis set so we decided not to include them in the present paper.

4.3. Binding energies

Full geometry optimization has been performed with analytical gradients of the total energy at SCF, MP2, and DFT [64–66] levels with all basis sets, except for 6-311++G(3df,3pd) where a single point calculation on the geometry optimized with the 6-311+(2d,2p) basis set has been carried out. For MP2 calculations with cc-pVTZ and aug-cc-pVTZ basis sets, only single-point calculations on the geometry optimized with the aug-cc-pVDZ basis set were carried out. Optimized geometries are not discussed here and are available from the authors upon request. Binding energies, BE, have been computed with the supermolecule approach, i.e. as the difference in the total energies between the complex and reference subunits at infinite distance. The basis set superposition error (BSSE) has been computed by the well known full counterpoise (CP) method [67]. Table 3 shows the BSSE for the FH/NH₃ adduct as a function of both basis set and method. Clearly, with basis sets belonging to the POL set the BSSE is sizeable and that associated to the DF methods is comparable to that from the MP2 calculations. However, with basis sets of the POLD set a significant reduction of the BSSE is shown for the DF methods, whereas the MP2 results are still significantly affected. Further details about BSSE can be found in ref. [25]. In the results section we will report the heat of formation of a given adduct at 0 K, $\Delta H^0(0)$, computed adding the harmonic zero point vibrational energy (ZPE) to the BE corrected for the BSSE.

4.4. Harmonic frequencies

The harmonic frequencies ω_h have been computed

Table 3

BSSE computed for the FH/NH₃ adduct with all methods and basis sets. Data in kJ/mol

Basis set	SCF	S-VWN	B-LYP	B-P86	B3-LYP	MP2
DZP	3	9	8	7	6	9
6-31G(d,p)	4	9	7	7	7	9
cc-pVDZ	10	19	19	17	17	17
cc-pVTZ	5	9	10	8	8	10
6-31+G(d,p)	4	6	5	5	5	9
6-311+G(d,p)	3	6	5	5	4	9
6-311+G(2d,2p)	1.5	2.5	2	2	2	6
6-311++G(3df,3pd)	2	2	1.7	1.6	1.6	5.5
aug-cc-pVDZ	2	3	3	2.6	2.6	6.4
aug-cc-pVTZ	0.4	0.5	0.3	0.3	0.3	2.8

by analytical second differentiation of the total energy and by standard solution of the equations of the nuclear motion [68] at all the levels of theory. Zero-point energy (ZPE) calculations have been carried out at the harmonic level only. We ensure, by calculating the full set of frequencies, that all obtained structures were minima on the potential energy surface.

4.5. Anharmonic analysis

A limited anharmonic analysis has been carried out for the F–H stretching frequency only for the free molecule as well as when engaged with both CO and NH₃ molecules. The following numerical procedure has been followed: (i) the F–H distance, assumed as a normal mode, was set to span a range of values around the equilibrium value obtained from the full geometry optimization at the corresponding level; (ii) the potential energy was calculated for each value of the F–H distance; (iii) a polynomial curve of sixth order was used to best fit the energy points, ensuring that the root mean square error was well below 10⁻⁶ hartree; (iv) the corresponding nuclear Schrödinger equation was solved numerically following the method proposed in ref. [69] by means of the program ANHARM [70]; (v) from the eigenvalues E_0 , E_1 and E_2 , $\omega_{01} = E_1 - E_0$ and $\omega_{02} = E_2 - E_0$, were computed; (vi) the anharmonicity constant $\omega_e x_e$ and the harmonic frequency ω_e are then defined as $\omega_e x_e = \omega_{01} - \omega_{02}/2$ and $\omega_e = \omega_{01} + 2\omega_e x_e$. Calculations have been done at the SCF, MP2, B-LYP and B3-LYP levels of theory with the 6-311+G(2d,2p) basis set. The starting geometries were those fully optimized at the

corresponding level. The separation between the centres of mass of FH and CO or NH₃ has been kept fixed at the original value computed for the fully optimized structure.

5. Results and discussion

Tables 4, 5 and 6 report the values of the heats of formation $\Delta H^0(0)$, the F–H frequency shift $\Delta\nu$ and the ratio $I_{FH}(\text{adduct})/I_{FH}(\text{free})$ between the infrared intensities of the F–H mode. Because of the large number of basis sets and methods involved for each of the three adducts, we have aggregated the results into two classes, named POL and POLD, respectively (see basis set section for details). For a given adduct and theoretical method, we compute the average value of a selected observable along with the corresponding standard deviation using the data obtained with all basis sets belonging to POL and POLD sets, respectively. The standard deviations are then a measure of the basis set dependency of the selected observable. Complete sets of results for each basis sets and method are available in the electronic form of this paper [25].

Before discussing in detail the results, we point out that both 6-31G(d,p) and cc-pVDZ basis sets are unreliable for studying the FH/FH adduct, because a cyclic geometry results during the optimization process at both DF and MP2 levels. This fact gives rise to spurious results, particularly for $\Delta H^0(0)$, as too low values were computed. On the contrary, both DZP and 6-31+G(d,p) do not suffer from the same shortcoming:

Table 4

Average heats of formation $\langle \Delta H^0(0) \rangle$ corrected for BSSE and corresponding standard deviations σ for all adducts obtained with data computed with POL^a and POLD^a sets, respectively. Data in kJ/mol

Adduct	Set	SCF	S-VWN	B-LYP	B-P86	B3-LYP	MP2
FH/OC	POL	2.2 ± 1	8.2 ± 1.4	0.23 ± 1.5	-1.23 ± 1.5	1.4 ± 1.3	-0.1 ± 1
	POLD	2.2 ± 0.8	10 ± 1	1.24 ± 1.0	-0.43 ± 1	2.1 ± 1	0.42 ± 1.0
FH/CO	POL	2.3 ± 0.8	24.2 ± 2	8.3 ± 2	7.8 ± 2	8.1 ± 2	5.9 ± 1.3
	POLD	2.1 ± 0.3	25.5 ± 0.5	7.5 ± 0.4	7.9 ± 0.5	7.6 ± 0.4	6.5 ± 0.9
FH/FH	POL	9.8 ± 1.0	24.8 ± 4	7.2 ± 5.5	6.2 ± 5.5	8.5 ± 5.2	7.4 ± 4
	POLD	8.9 ± 0.8	26.6 ± 0.4	10 ± 0.7	9 ± 0.5	11.2 ± 0.7	9.4 ± 0.8
FH/NH ₃	POL	30.7 ± 3	68 ± 5	39.9 ± 5	42.2 ± 4.5	41.3 ± 4.4	34.7 ± 3.6
	POLD	29.1 ± 1.4	73 ± 2	42 ± 1.7	44.7 ± 1.5	42.4 ± 1.7	36.8 ± 2

^a See basis set section for the definition of POL and POLD sets.

for instance, values of 4.0, 4.1, 14.2 and 12.2 kJ/mol are computed at B3-LYP with cc-pVDZ, 6-31G(d,p), DZP and 6-31+G(d,p), respectively (the best value is 11.1 kJ/mol with aug-cc-pVTZ).

5.1. Heats of formation

Table 4 collects the average value of the heats of formation $\langle \Delta H^0(0) \rangle$ with the corresponding standard deviations for all adducts. These data show a marked overestimation of the $\Delta H^0(0)$ value computed for all adducts using the local density functional S-VWN when compared to the results computed with all other DF methods as well as with the MP2 method.

As far as basis set dependency of the heats of formation, it is worth noting that standard deviations at the MP2 level are as large as those computed with all the DF methods, showing a similar sensitivity to basis set quality of the two approaches. The anomalously large values of the standard deviations for the FH/FH adduct associated with the POL set are the

consequence of the poor performance of both 6-31G(d,p) and cc-pVDZ basis sets, as described in the previous section.

Heats of formation computed for the POLD set are slightly larger than those for the POL set, showing the sensitivity of the binding energy for H-bonded adducts to the presence of diffuse functions.

The energetics of the FH/CO and FH/OC adducts has been studied in the past by many researchers, because well correlated treatments are needed to compute the former conformer as the most stable one. Indeed, data in Table 4 show the notoriously wrong behaviour of the SCF method, which yields the two conformers as almost isoenergetic (for a possible explanation, see ref. [23]), whereas all DF and MP2 methods gave the correct order of stability, preferring the C-bound conformer.

Comparison of the data with those reported in Table 2 shows a remarkable agreement between DF results (with the obvious exclusion of the S-VWN data) and those computed with the more sophisticated post-SCF

Table 5

Average F–H harmonic frequency shifts $\langle \Delta \nu \rangle$ and corresponding standard deviations σ for all adducts obtained with data computed with POL and POLD sets. Data in cm⁻¹

Adduct	Set	SCF	S-VWN	B-LYP	B-P86	B3-LYP	MP2
FH/OC	POL	17 ± 6	83 ± 20	18 ± 11	36 ± 11	18 ± 9	1 ± 6
	POLD	27 ± 4	130 ± 10	46 ± 7	60 ± 4	45 ± 7	22 ± 8
FH/CO	POL	65 ± 9	329 ± 36	169 ± 25	217 ± 25	151 ± 19	96 ± 14
	POLD	79 ± 7	434 ± 15	234 ± 13	286 ± 15	204 ± 12	149 ± 23
FH/FH	POL	88 ± 6	362 ± 49	187 ± 8	220 ± 9	155 ± 7	113 ± 9
	POLD	87 ± 7	325 ± 20	175 ± 15	210 ± 16	159 ± 16	114 ± 21
FH/NH ₃	POL	463 ± 32	898 ± 95	679 ± 87	758 ± 86	670 ± 72	563 ± 77
	POLD	535 ± 14	1200 ± 20	936 ± 27	1020 ± 18	879 ± 27	767 ± 49

Table 6

Average ratio $\langle I/I_0 \rangle$ between infrared intensity I of the F–H stretch mode in the adduct and the same quantity I_0 for the free FH molecule with the corresponding standard deviations σ for all adducts obtained with data computed with POL and POLD sets

Adduct	Set	SCF	S-VWN	B-LYP	B-P86	B3-LYP	MP2
FH/OC	POL	2.2 ± 0.1	6.2 ± 1	5 ± 1	4.5 ± 0.7	4 ± 0.5	2.9 ± 0.2
	POLD	2.1 ± 0.1	5.2 ± 0.4	3.4 ± 0.2	3.4 ± 0.2	3.1 ± 0.1	2.6 ± 0.2
FH/CO	POL	2.7 ± 0.2	8.6 ± 1.1	8.9 ± 1.5	8.4 ± 1.0	6.4 ± 0.8	4.6 ± 0.3
	POLD	2.6 ± 0.2	8.2 ± 0.5	6.9 ± 0.4	7.4 ± 0.5	5.6 ± 0.3	4.4 ± 0.4
FH/FH	POL	2.8 ± 0	6.3 ± 1	6.1 ± 1.1	5.8 ± 1	4.6 ± 0.8	3.7 ± 0.3
	POLD	2.7 ± 0.1	6.2 ± 0.5	5.0 ± 0.4	5.3 ± 0.5	4.3 ± 0.3	3.6 ± 0.3
FH/NH ₃	POL	6.7 ± 0.4	17.9 ± 2.2	21.4 ± 3.6	19.9 ± 2.5	15.4 ± 1.8	11.4 ± 1.1
	POLD	7.1 ± 0.3	17.5 ± 1.1	18.5 ± 1.2	19.3 ± 1.2	14.8 ± 0.9	12.4 ± 1.4

methods (CCSD(T) and MP n) as well as with the experimental results. The worst agreement is for the FH/OC adduct, for which a too low value of $\Delta H^0(0)$ is computed with the gradient-corrected DF methods.

5.2. Harmonic frequencies

The frequency shift of the F–H stretching mode as caused by the hydrogen bond interaction is a relevant quantity which is easily accessible from IR experiments either in cold gas matrices or in the gas phase. Its magnitude is a function of the energy of interaction, so that the $\Delta\nu(\text{FH})$ value has been computed here at both harmonic and anharmonic levels. Table 5 shows $\langle \Delta\nu \rangle$, the average harmonic F–H frequency shift with the corresponding standard deviations σ computed with the same method described in the previous section. As was the case for the heats of formation, the magnitude of the F–H shifts are also grossly overestimated by the S-VWN method, being more than twice as large as the values computed with gradient corrected DF methods. The magnitude of the shift follows the sequence S-VWN \gg B-P86 > B-LYP > B3-LYP > MP2 > SCF. Standard deviations for the POLD set are larger for MP2 results than for all the DF methods, showing a larger basis set dependence of the traditional post-SCF methods for computing frequency shifts. Comparison with the data from Table 2 shows that DF $\Delta\nu$ values are overestimated with respect to both computed and experimental data. The disagreement appears even more serious considering that the computed shifts are at the harmonic level whereas experimental values include, obviously, anharmonicity. On the other hand, the harmonic MP2 shifts show a better trend, being instead

slightly underestimated in comparison with the experiment. A more thorough analysis will be given in a subsequent section devoted to the influence of anharmonic corrections to $\Delta\nu(\text{FH})$.

5.3. Infrared intensities

The increase in the infrared intensity associated with the F–H stretch was due to the hydrogen bond established with the base molecule, this is one of the fingerprints of such an interaction. Experimental determinations of the absolute IR intensities are hampered by technical difficulties. However, from the analysis of a large number of spectra, it has been shown that the intensification of the F–H stretch by hydrogen bond formation follows the strength of interaction and may be in the range between 2 to 20 times the value of the unperturbed FH molecule.

Table 6 shows the computed ratios using the same averaging described in the previous sections. Basis set dependency is in general small; S-VWN data, contrary to the previous discussion, are no longer overestimated with respect to the rest of data. Among DF results, the B3-LYP values are the closest to the MP2 ones, even if they are on the high side. The only available data for comparison results in 4.2 computed at CCSD(T)/TZ2p(f,d) level for the FH/FH dimer [27]: this is in excellent agreement with the average B3-LYP value of 4.3 ± 0.3 obtained with the POLD set.

5.4. Anharmonic FH frequencies

To study in deeper detail the anharmonicity of the FH stretch, the numerical procedure described in the

Table 7

Computed and experimental vibrational features of the free FH molecule. Basis set is 6-311+G(2d,2p). Gas-phase measurements indicated as *gp*; cold gas matrices measurements labelled with the corresponding atomic symbol. See text for symbols definitions

Quantity	SCF	B-LYP	B3-LYP	MP2	MP4 ^d	CCSD(T) ^d	Exp.
ω_h	4492	3949	4100	4165			4138.3 ^a
ω_e	4484	3981	4089	4157	4111.0	4141.9	4139 ^a
ω_{01}	4322	3763	3923	3988	3934.2	3966.3	3961 (gp) ^b 3954 (Ar) ^c
ω_{02}	8481	7358	7677	7806	7691	7757	
$\omega_e x_e$	81.3	84	83	84.8	88.4	87.8	89.9 ^a

^a Ref. [40]. ^b Ref. [41]. ^c Ref. [34,42]. ^d With aug-cc-pV5Z basis set [2].

method section has been carried out for the FH/CO and FH/NH₃ adducts. Four methods have been used, namely SCF, MP2, B-LYP and B3-LYP with the 6-311+G(2d,2p) basis set. Results are shown in Table 7 for the isolated FH molecule and in Table 8 for the adducts. Results for the adducts are affected by the approximation of the numerical procedure, in particular the decoupling of the F–H mode from all the other vibrational modes. However, because of the small coupling between the high frequency F–H stretch and the low frequency intermolecular modes, we expect only small corrections to our final results.

Data in Table 7 shows that values of ω_h , ω_e and ω_{01}

computed with both B3-LYP and MP2 are in excellent agreement with experiment, the former being systematically underestimated. Corresponding B-LYP data are, instead, much lower than the experimental determination, particularly for the ω_{01} .

In all cases, ω_h , ω_e and ω_{01} at correlated levels are, however, a vast improvement with respect to the SCF estimate. The anharmonicity constant, $\omega_e x_e$, is curiously enough almost insensitive to electron correlation, as shown by the minute increase of the SCF values upon introduction of electron correlation.

Table 8 shows the data obtained for the FH/CO adduct. The contribution due to the anharmonicity

Table 8

Computed and experimental vibrational features of the F–H stretch mode in the FH/CO and FH/NH₃ adducts. Basis set is 6-311+G(2d,2p). $\Delta\omega_e$, $\Delta\omega_{01}$ and $\Delta\omega_h$ are shifts in the F–H stretch with respect to the value for the free molecule. Data in cm⁻¹

Adduct	Quantity	SCF	B-LYP	B3-LYP	MP2	Exp.	
FH/CO	ω_h	4413	3717	3900	4008		
	ω_e	4408	3706	3888	4005		
	ω_{01}	4222	3482	3673	3794	3844 (gp) ^a 3789 (Ar) ^b	
	$\omega_e x_e$	93	112	108	106		
	$\Delta\omega_h$	79	225	200	158		
	$\Delta\omega_e$	76	225	201	152		
	$\Delta\omega_{01}$	100	281	250	194	117 (gp) ^a 165 (Ar) ^b	
	$\Delta\omega_e x_e$	12	28	25	21		
	FH/NH ₃	ω_h	3963	3030	3240	3430	
		ω_e	3994	3024	3257	3445	
ω_{01}		3648	2675	2865	3074	3041 (Ar) ^c	
$\omega_e x_e$		173	175	196	185		
$\Delta\omega_h$		529	912	860	735		
$\Delta\omega_e$		490	902	832	712		
$\Delta\omega_{01}$		673	1089	1058	913	912 (Ar) ^c	
$\Delta\omega_e x_e$		92	91	113	100		

^a Ref. [39]. ^b Ref. [41]. ^c Ref. [33].

of the FH frequency shift is sizeable at all levels of theory, the harmonic $\Delta\omega_h$ values being increased by almost 25%. Comparison with the available experimental results show an excellent agreement of the MP2 data even if the $\Delta\omega_{01}$ value is slightly overestimated. DF methods, all significantly overestimate $\Delta\omega_{01}$ with noticeably bad performance from the B-LYP method.

The anharmonicity of the free F–H mode is, in all cases, increased by the formation of the H-bonded adducts, as shown by a 30% increase in the $\omega_e x_e$ term.

The same remarks as were made for the FH/CO adduct hold for the FH/NH₃ adduct, with MP2 $\Delta\omega_{01}$ in excellent agreement with experiment, the SCF value being too low and all the DF methods overshooting the experimental measurements. Worthy of note, is the anharmonicity increase of the F–H mode, which is almost doubled with respect to the value for the free FH molecule by the formation of the adduct. Comparison with the data for the FH/CO adduct seems to suggest that anharmonicity increment parallels the interaction energy.

6. Conclusions

From the previous results section a number of conclusions are possible:

1. the S-VWN method greatly overestimates both binding energies and the shift in the FH donor stretching mode with respect to both gradient corrected and MP2 methods. Intermolecular distances are largely underestimated as a consequence of the extra-binding when compared to MP2 and other gradient corrected DF methods. Non-gradient corrected DF methods should then be avoided as a method of choice to study hydrogen bond interactions.
2. B-LYP and B3-LYP values of the heats of formation are very close to each other and represent a definite improvement with respect to SCF results. The value of 11.1 kJ/mol computed at B3-LYP/aug-cc-pVTZ for the FH/FH adduct is in excellent agreement with both the experimental measurement of 12.70 ± 0.012 kJ/mol [28] and the value of 12.3 kJ/mol computed at CCSD(T)/TZ2P(f,d) by Schaefer III and coworkers [27].
3. B-LYP and B3-LYP shifts in FH frequency are significant different from each other and are, for both cases, larger than the shifts computed at the MP2 level for all the considered adducts. The shift of 174 cm^{-1} computed for the FH/FH adduct at B3-LYP/aug-cc-pVTZ is significantly larger than both the value of 107 cm^{-1} computed at CCSD(T)/TZ2P(f,d) level by Schaefer III and coworkers [27] and the experimental determinations in the gas-phase and in matrix of 93 [29], 105 [30] and 128 cm^{-1} [31].
4. Anharmonicity analysis (see anharmonic section) shows definitely that B-LYP and B3-LYP overestimate the FH frequency shift when compared to both experiment and MP2 results. However, due to Hartree–Fock mixing of the exchange part of the B3-LYP functional, the overestimation associated with this method is less severe also at the harmonic level. We feel that the reason for such behaviour is due to the incomplete cancellation of the self-interaction affecting the present DF methods, which is particularly relevant for hydrogen containing bonds.
5. Standard deviations of both heats of formation and frequency shifts associated with the MP2 method are larger with respect to gradient corrected DF methods showing a larger basis set dependency of the former.
6. DF and MP2 methods when used with the popular 6-31G(d,p) basis set may give rise to spurious results: a clear example is the FH/FH dimer for which a cyclic conformation is obtained. The intermolecular geometry for all other adducts is in agreement with those obtained by others (see Table 1).
7. Adding diffuse *sp* functions greatly improves the performance of small polarized basis sets like 6-31G(d,p) and cc-pVDZ. The relatively small basis set 6-31+G(d,p) is the recommended choice if very large hydrogen bonded systems have to be studied computationally.
8. The performances of the DF methods associated to the aug-cc-pVDZ, aug-cc-pVTZ and 6-311+G(2d,2p) basis sets are very similar to each other and the latter is recommended when computer resources are limited.
9. Basis set superposition error associated with the DF methods is definitely smaller when compared to that computed for the MP2 method. With the POLD set the BSSE virtually disappear, being less than 2 kJ/mol at B3-LYP/aug-cc-pVTZ.

10. The intensification of the infrared intensity associated with the F–H stretching mode caused by hydrogen bonding is dramatically enhanced by all DF methods with respect to the SCF value. The value of 4.5 computed for the FH/FH adduct at B3-LYP/aug-cc-pVTZ is in excellent agreement with the value of 4.2 reported by Schaefer and coworkers at the CCSD(T)/TZ2p(f,d) level [27].

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