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Equilibrium structure of the hydrogen bonded dimer $H_2O \cdots HF$.

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Proposed running-head: structure of $H_2O \cdots HF$

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Abstract

The equilibrium structure of the hydrogen bonded complex $H_2O \cdots HF$ has been calculated ab initio using the CCSD(T) method with basis sets up to sextuple-ζ quality with diffuse functions and taking into account the basis set superposition error correction. The calculations carried out confirm the importance of diffuse functions and of counterpoise correction to obtain an accurate geometry. The most important point is that the basis set convergence is extremely slow and, for this reason an accurate ab initio structure requires a very large basis set. Nevertheless, the ab initio structure is significantly different from the experimental r_0 and r_m structures. Analysis of the basis set convergence and of the approximations used for the determination of the experimental structures indicates that the *ab initio* structure is expected to be more reliable.

Keywords: ab initio, structure, hydrogen bond, $H_2O \cdots HF$.

1. Introduction

The hydrogen-bonded heterodimer $H_2O \cdots HF$ has been observed in gas phase for the first time in 1975 by infrared spectroscopy [1]. The same year, its rotational spectrum was measured [2]. Then, its microwave spectrum was analyzed in great detail by Kisiel, Legon, Millen *et al.* permitting the determination of its effective (r_0) structure [3, 4], dipole moment [5], harmonic force field [6] and dissociation energy [7]. It was established that the equilibrium configuration at the oxygen atom is pyramidal (C_s symmetry) with a double minimum potential (see Figure 1). More recently, its submillimeterwave spectrum has been investigated [8] and its empirical mass-dependent r_m structure determined [9].

This dimer has been subject to many ab initio calculations leading to three important conclusions [10, 11, 12] : i) the nondynamical electron correlation is small ii) the basis set superposition error (BSSE) is large iii) the convergence of the basis sets is slow. However, most of these calculations are devoted to the determination of dynamical properties (potential barrier, dissociation energy, …) and there is no very high level calculation of the geometrical structure.

The goal of this work is threefold : i) to determine a reliable ab initio equilibrium structure at a high level of theory using basis sets as large as possible and to compare it to the

experimental structures ii) to check the structural changes upon dimerization because it is often assumed that the geometry of the monomers does not change upon dimerization iii) to check the performance of density functional theory (DFT) for the calculation of the structure of hydrogen-bonded complexes because it seems that some popular functionals perform rather poorly [13]. This is important, because the procedure used here to determine the ab initio structure of $H_2O \cdots HF$ cannot be used for larger molecules. Using DFT would thus be an interesting alternative, whose accuracy is still to be checked.

2. Methods of computation

Most correlated-level *ab initio* electronic structure computations of the present study have been carried out at two levels: second-order Møller–Plesset perturbation theory (MP2) [14] and coupled cluster (CC) theory with single and double excitation [15] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [16]. The Kohn–Sham density functional theory [17] was also used in this study using a variety of functionals as described in section 4.

We used correlation-consistent polarized *n*-tuple zeta basis sets cc-pV*n*Z [18] with $n \in$ {D, T, Q, 5, 6}, that are abbreviated as V*n*Z in the text. For hydrogen-bonded complexes, the inclusion of diffuse functions in the basis set is important. For this reason, the augmented V*n*Z (aug-cc-pV*n*Z, AV*n*Z in short) basis sets [19] were employed. The effect of adding a second set of diffuse functions has also been investigated by using the doubly augmented V*n*Z (d-aug-cc-pV*n*Z, dAV*n*Z in short) basis sets. For some DFT calculations, the Jensen's polarization consistent basis set with diffuse functions apc*n* ($n = 2, 3, 4$) was used [20].

The core-core and core-valence correlation effects on the computed equilibrium geometries [21], were estimated thanks to the correlation-consistent polarized weighted core-valence quadruple zeta (cc-pwCVQZ) [22,23] basis sets. In principle, for first-row atoms, it is sufficient to use the MP2 method to estimate this correction [24]. The frozen core approximation (hereafter denoted as *fc*), *i.e.*, keeping the 1s orbitals of F, and O doubly occupied during correlated-level calculations, was used extensively. Some geometry optimizations were also carried out by correlating all electrons (hereafter denoted as *ae*).

The CCSD(T) calculations were performed with MOLPRO [25,26, 27] electronic structure program packages while most other calculations utilized the GAUSSIAN03 (g03) program [28]. The basis set superposition error (BSSE) was taken into account by the

counterpoise correction (CP) [29]. Most calculations were performed on the HP-XC4000 cluster of the ULB/VUB computing center.

3. Ab initio results

The first interesting result is the value of the T_1 diagnostic [30] calculated at the CCSD(T) level whose value is 0.0069 with the wCVQZ(ae) basis set and 0.0092 with the AV5Z basis set. These values are much smaller than the cut-off value of 0.020 and thus confirm that the single-reference CCSD(T) method is well appropriate for properly describing electron correlation effects.

The equilibrium geometries obtained at MP2 level with and without CP corrections are reported in Table 1. The geometrical parameters can be visualized in Figure 1 (see also the legend for the definition of α and β). The first point to be noted is the large effect of the diffuse functions on the distances between non-bonded atoms O···H (F···O), but also on the H-F bond length. At the VQZ level, addition of a single set of diffuse functions decreases the $r(\text{O}\cdots\text{H})$ bond length by as much as 0.0033 Å, while at the V5Z level, the decrease is only of 0.0004 Å. On the other hand, it is found that the addition of a second set of diffuse functions is still important at the VTZ level (decrease of $r(\text{O}\cdots\text{H})$ by 0.0019 Å from AVTZ to dAVTZ, but that the corresponding effect is negligible for larger n values (0.0003 Å on $r(\text{O}\cdots\text{H})$ at V5Z). Another important point is the effect of the CP correction, which is quite large for the $r(\text{O}\cdots\text{H})$ bond length and for small basis sets. It is still important with the AV5Z basis set, the O···H bond length increasing by 0.0069 Å. Figure 2 shows the convergence of the O···H and O···F bond lengths as a function of the cardinal number of the basis set for the MP2 calculations with and without CP correction. It appears that the convergence is more regular when the CP correction is taken into account but it remains slow. For the O···H bond length, it is obviously not yet achieved at the AV5Z level. However, if we extrapolate $r(\text{O}\cdots\text{H})$ to complete basis set (CBS) using a simple polynomial of the form

$$r_n = r_{\text{CBS}} + an^{-3} \tag{1}$$

as suggested by Paizs et al. [11] and only using the AVQZ and AV5Z results (i.e. $n = 4$ and 5), the result is almost the same with and without CP correction: $r_{\text{CBS}} = 1.7116$ Å to be compared with $r_{\text{CBS}}^{\text{CP}} = 1.7102$ Å. As a check, the $r(\text{O}\cdots\text{H})$ bond length was optimized at the MP2/AV6Z level of theory with the CP correction, all other parameters being fixed at their

MP2/AV5Z + CP value. The result $r(O\cdots H) = 1.7112$ Å confirms the validity of the extrapolation.

The CCSD(T) results are given in Table 2 for basis sets AVnZ with n = D, T, Q, 5, and the convergence curve is shown on Figure 2 for comparison with the corresponding MP2 results. Each parameter is extrapolated to CBS using Eq. (1) and the AVQZ and AV5Z results. When the CP correction is taken into account at the AV5Z level, r(F$\cdots$O) = 2.652 Å to be compared with the CBS value which is r(F$\cdots$O) = 2.651 Å. It again confirms the reliability of the extrapolated value. It is worth noting that the CP correction is larger when calculated at the MP2 level: the CP correction increases the $r(O\cdots H)$ bond length by 0.0069 Å at the MP2/AV5Z level of theory while this increase is only of 0.0045 Å at the CCSD(T)/AV5Z level.

Finally, the core correction was calculated at the CCSD(T) and MP2 levels with and without CP correction. The regular wCVQZ basis set as well as the augmented AwCVQZ basis set were used. The effect of the CP correction was also investigated, see Table 3. The conclusion is that, to calculate the core correction, it is not necessary to take into account the CP correction, and it is sufficient to use the non-augmented wCVQZ basis set. Finally, the MP2 and CCSD(T) methods give similar results, the MP2 value being slightly larger (by 0.0004 Å) for the F$\cdots$O distance. Likewise, for the $r(O\cdots H)$ bond length, the core correction is 0.0024 Å at the MP2 level and 0.0019 Å at the CCSD(T) level. It is also worth to be noted that the core correction is large for the angle β.

The best estimate of the equilibrium structure is obtained by correcting the CCSD(T)/CBS structure for the effects of core correlation calculated at the CCSD(T)/wCVQZ level. The extrapolation to CBS is not expected to be highly accurate. The equilibrium structure is given in Table 4 where it is compared to the previous calculations and to the experimental empirical structures as well as to the equilibrium structures of the monomers. The equilibrium value for the F$\cdots$O distance is 2.649 Å, it is slightly shorter than the previous ab initio estimate [11] which gave 2.652 Å and it is much shorter than the experimental empirical structures. It has already been observed that the variation of the rovibrational contribution $\varepsilon = I_0 - I_e$ upon isotopic substitution is much larger in complexes than in rigid molecules [31] mainly because they are inversely proportional to vibrational frequencies, some of them being very low in complexes. The basic assumption of the r_0 structure is that ε is negligible while the basic assumption of the substitution (r_s) structure is that ε remains constant upon isotopic substitution. Obviously, neither assumption is valid in

the particular case of complexes. It explains the failure of these empirical methods. On the other hand, the r_m method assumes that ε varies as the square root of the moment of inertia [32]:

$$\varepsilon_g = c_g \sqrt{I_g} \qquad g = a, b, c \tag{2}$$

This gives the $r_m^{(1)}$ method. However, for XH bonds (here X = F, O), it is necessary to take into account the variation of the bond length upon deuteration, called Laurie correction. Watson et al. [33] assume that the apparent bond X-H and X-D consist of a common part r_m which is identical for both bonds (and assumed to be close to r_e) plus an additional bond elongation due to the H or D atom asymmetrically vibrating against the rest of the molecule. This elongation is taken proportional to the respective frequency, i.e. proportional to the reciprocal square root of the reduced mass of the vibrator. In other words, the X-H bond length is given by:

$$r_m^{\text{eff}}(\text{XH}) = r_m(\text{XH}) + \delta \left[\frac{M}{m_H(M - m_H)} \right]^{1/2} \tag{3}$$

where δ is an adjustable parameter, M is the total mass of the molecule and m_H the mass of hydrogen (or deuterium).

A simple way to check the validity of Eq. (3) is to plot ε as a function of $\sqrt{I}$. As $H_2O\cdots HF$ is a near-symmetric top, the A rotational constant could not be determined for its isotopologues. Furthermore, it is possible to define a mean rotational constant $\overline{B} = (B + C)/2$ and a mean moment of inertia $I = h^2/8\pi^2\overline{B}$. ε is then calculated using the experimental ground state rotational constants [3] and the equilibrium structure of Table 4. A nice, almost linear relationship is found for the deuterated species with an almost parallel line for the non-deuterated species, see Figure 3. It was expected to obtain different correlations for the deuterated and non-deuterated species because of Laurie correction, Eq. (4). This confirms the conclusion of Kisiel [9] that the r_m method can be used for H-bonded complexes. However, the accuracy of the r_m structure of $H_2O\cdots HF$ is limited by several factors: i) there is no isotopic substitution for fluorine ii) the coefficients c_b of Eq. (3) and δ are fully correlated. These two factors severely limit the accuracy of the experimental r_m structure and may explain the difference found with the r_e structure of Table 4.

Finally, the comparison of the structure of the dimer to those of the monomers shows that the H_2O moiety is not too much affected by the formation of the hydrogen bond (the $\angle$(HOH) bond angle increases by 1.1° only and the r(OH) bond length is almost constant).

The traditional assumption of unchanged monomer geometries does not apply however for the HF moiety, the HF bond length being lengthened by as much as 0.156 Å.

Since the counterpoise correction was carried out for most calculations, the dimerisation energy is easy to determine. It is listed in table 1 for the MP2 calculations. For the CCSD(T)/AV5Z level of theory, it is $\Delta E = -37.54$ kJ/mol. This value is slightly smaller (in absolute value) than the MP2 value (Table 1). As the dimerisation energy decreases (in absolute value) with the size of the basis set, the CBS value is expected to be close to -36 kJ/mol. Indeed, Halkier *et al.*[10] found $\Delta E = -35.61$ kJ/mol using a two-points extrapolation. This result is in good agreement with the value found by Boese *et al.*[34] using the W2 theory: $\Delta E = -36.35$ kJ/mol but it is significantly different of the experimental value: $\Delta E = -42.68$ kJ/mol.[7] However, this last value was obtained from the zero-point dissociation energy, $D_0 = 34.3(3)$ kJ/mol, which seems to be compatible with the *ab initio* values. The observed discrepancy might be explained by the difficulty to estimate a meaningful zero-point energy for a floppy molecule with a double minimum potential.

4. DFT results

Calculations with the CCSD(T) method and very large basis sets (up to AV5Z), like those presented in the previous section, cannot be carried out for molecules much larger than $H_2O \cdots HF$. For this reason, it would be useful to check the accuracy of more approximate methods. $H_2O \cdots HF$ is indeed a fairly strongly bond complex with dominant electrostatic contribution to the binding energy and a relatively unimportant dispersive term.

First, it is interesting to note that the MP2 and CCSD(T) methods give similar values for the $F \cdots O$ distance.

It is also useful to make a comparative study of the results obtained with the density functional (DFT) methods. They are indeed widely used, mainly because of their relatively low cost. There is already a large amount of papers on this subject. For instance Tuma et al. [33] compared the results of CCSD(T) calculations with those of a large variety of density functionals. Their work was recently extended to other density functionals by Boese et al. [34]. However, in both cases, the reference structure was calculated with the AVQZ basis set. In other words, this structure may be significantly different from the equilibrium geometry because the convergence of the basis set is not achieved. One difficulty is that the world of DFT methods is becoming a jungle of acronyms corresponding to choices of parameters more

7

or less ad hoc. Nevertheless, among the numerous exchange-correlation functionals currently used, one should consider:

- B3LYP, Becke 3-parameter [35] Lee–Yang–Parr [36] hybrid functional which is extremely popular and is known to give reliable results in many cases [37] although its accuracy for hydrogen bonds is disputed [13].

- BLYP, Becke-Lee-Yang-Parr functional which uses the Becke 88 [38] exchange and the LYP [37] correlation functional and which is often employed when calculating hydrogen bonds [34]. Furthermore, Jensen's [21] apc$n$ basis sets have been optimized for this functional.

- PW91, Perdew and Wang's exchange and correlation functional [39] which was shown to perform much better than the BLYP and B3LYP functionals for the prediction of intermolecular interaction energies [13].

A number of second-generation functionals have been proposed as successors. The most successful ones are:

- B97-1, reparametrization of Becke's B97 Functional [40] by Handy et al. [41]

- BMK, Boese-Martin for Kinetics [42] which was found to perform well for hydrogen-bonded complexes.

A big advantage of the DFT methods is that, as shown by Boese et al. [43, 44], a basis set of triple zeta quality is sufficient. They also showed that Pople's 6-311+G(3df,2pd) basis set [45] performs quite well for DFT calculations. This confirms the conclusion of Bauschlicher et al. [38] who found that this basis set is better than the AVTZ one. However, as a check, for some calculations, the AVTZ and Jensen's apc2 and apc3 basis sets were also used. In most cases, the CP correction was taken into account. The results are given in Table 5.

As expected, the best results are obtained with the 6-311+g(3df,2pd) basis set and with the B97-1 and BMK methods which confirms the conclusions of Boese et al. [43, 45]. However, they are not more accurate than with the MP2 method; this is particularly true for the angles. In particular β values spread over a range as large as 11°, while for MP2 and CCSD(T) this range does not exceed 3°. This angle which is very sensitive to the level of theory is a good indicator of the quality of the calculation. A similar scattering is also observed for the DFT F…O and H…O distances (up to 0.050 Å) while MP2 and CCSD(T) values only change by less than 0.02 Å. Finally, it has to be noted that, for the dimerisation energy, the DFT methods are less accurate than the MP2 method. For instance, for the B97-1/apc3 level of theory, it is ΔE = –38.55 kJ/mol

5. Barrier height

The potential energy function governing the out-of-plane bending mode is of the double minimum type. The potential barrier between the pyramidal minimum and the planar top ($\beta = 0$) of the barrier was determined experimentally by Kisiel *et al.* [4] to be $V = 126$ cm^{-1} (1.5 kJ/mol). The barrier was calculated at the CCSD(T)/AV5Z level of theory giving $V = 115$ cm^{-1} in good agreement with the experimental value. The effect of the core correlation is small, decreasing the barrier by only 6 cm^{-1}. The effect of the zero point energy is more difficult to estimate because of the double minimum nature of the potential. Furthermore, at the AV5Z level, the CCSD(T) energy is not yet completely converged. In conclusion, the good agreement between the experimental and the *ab initio* values is likely to be due to a compensation of errors.

6. Conclusions

Geometry optimizations were carried out for the $H_2O \cdots HF$ complex using the CCSD(T), MP2, and some DFT methods and with large basis sets (up to AV6Z). The bond lengths and angles were extrapolated to the CBS limit with and without the CP correction. The core correlation was also taken into account.

For the hydrogen bond distance $r(H \cdots O)$, the MP2 method gives a result close to the value found at the CCSD(T) level. On the other hand, the different DFT methods give a large scattering of values, B97-1 appearing to be the best one, although inferior to MP2.

Our best estimate of the structure has been obtained from the CCSD(T)/CBS results corrected for core correlation effects. A comparison between the CBS and the AV5Z results indicate that the accuracy is probably better than 0.003 Å for the $r(F \cdots O)$ and the $r(O \cdots H)$ bond lengths. For the other bond lengths, the accuracy is thought to be better than 0.002 Å and for the bond angles, it is of the order of 0.1°. This *ab initio* structure is expected to be more reliable than the published experimental ones whose accuracy is limited by several factors analyzed in detail in this work.

Upon formation of the hydrogen bond, the intramolecular OH distance is not significantly affected, the $\angle(HOH)$ bond angle increases by 1.1° and the intramolecular HF bond length experiences a rather large elongation of 0.156 Å.

Table 1. MP2 structures for $H_2O\cdots HF$ (distances in Å, angles in degrees and dimerisation energy in kJ/mol).

basis set	r(OH)	r(HF)	r(F$\cdots$O)	$\angle\alpha$	$\angle$(HOH)	$\angle\beta$	r(O$\cdots$H)	ΔE [a]
VTZ	0.9607	0.9344	2.6426	2.308	104.655	126.355	1.7094	
VQZ	0.9591	0.9344	2.6407	1.747	105.071	129.468	1.7070	
V5Z	0.9591	0.9354	2.6428	1.491	105.307	132.130	1.7079	
AVDZ	0.9668	0.9427	2.6575	1.398	104.684	129.522	1.7152	
AVTZ	0.9625	0.9398	2.6432	1.446	105.093	130.684	1.7039	
AVQZ	0.9599	0.9367	2.6400	1.424	105.283	132.365	1.7037	
AV5Z	0.9594	0.9361	2.6432	1.439	105.353	132.391	1.7075	
dAVDZ	0.9670	0.9424	2.6495	1.226	104.667	128.621	1.7075	
dAVTZ	0.9626	0.9401	2.6416	1.550	105.056	129.926	1.7020	
dAVTZ + CP	0.9624	0.9393	2.6610	1.466	105.070	131.841	1.7222	−38.69
dAVQZ	0.9600	0.9368	2.6404	1.413	105.268	131.797	1.7041	
dAV5Z	0.9595	0.9361	2.6434	1.465	105.358	132.314	1.7078	
AVDZ + CP	0.9669	0.9406	2.7008	1.485	104.716	130.595	1.7606	−38.34
AVTZ + CP	0.9623	0.9389	2.6615	1.437	105.093	131.986	1.7231	−38.32
AVQZ + CP	0.9599	0.9359	2.6538	1.445	105.264	132.602	1.7184	−38.08
AV5Z + CP	0.9594	0.9357	2.6497	1.458	105.369	132.627	1.7144	−37.74

[a] ΔE = dimerisation energy.

Table 2. CCSD(T) structures for $H_2O\cdots HF$ (distances in Å and angles in degrees).

basis set	r(OH)	r(HF)	r(F$\cdots$O)	$\angle\alpha$	$\angle$(HOH)	$\angle\beta$	r(O$\cdots$H)
AVDZ	0.9672	0.9403	2.6646	1.593	104.723	129.007	1.7249
AVTZ	0.9625	0.9372	2.6477	1.653	105.137	130.090	1.7111
AVQZ	0.9598	0.9341	2.6446	1.638	105.357	131.904	1.7110
AV5Z	0.9593	0.9335	2.6477	1.632	105.420	132.030	1.7147
CBS	0.9588	0.9329	2.6509	1.626	105.490	132.160	1.7186

Table 3. Calculation of the core correlation for $H_2O\cdots HF$ (distances in Å and angles in degrees).

method [a]		r(OH)	r(HF)	r(F···O)	∠α	∠(HOH)	∠β	r(O···H)
MP2/wCVQZ	fc	0.9592	0.9344	2.6419	1.739	105.082	129.833	1.7082
	ae	0.9583	0.9339	2.6391	1.725	105.219	130.360	1.7059
fc - ae		0.0009	0.0005	0.0028	˜13	−0.137	−0.526	0.0023
MP2/AwCVQZ	fc	0.9599	0.9367	2.6422	1.410	105.300	132.594	1.7059
	ae	0.9590	0.9362	2.6393	1.410	105.438	133.104	1.7035
fc - ae		0.0009	0.0005	0.0029	˜	−0.138	−0.510	0.0024
MP2/wCVQZ+CP	fc	0.9587	0.9330	2.6657	1.226	105.088	135.503	1.7330
	ae	0.9578	0.9325	2.6628	1.208	105.226	136.105	1.7306
fc - ae		0.0009	0.0005	0.0029	˜18	−0.138	−0.602	0.0024
CCSD(T)/wCVQZ	fc	0.9591	0.9318	2.6464	1.743	105.206	131.459	1.7153
	ae	0.9582	0.9313	2.6440	1.730	105.332	131.966	1.7134
fc - ae		0.0009	0.0005	0.0024	˜13	−0.126	−0.506	0.0019

[a] fc = frozen core approximation; ae = all electrons correlated.

Table 4. Structures of $H_2O \cdots HF$ (distances in Å and angles in degrees).

	r(OH)	r(HF)	r(F$\cdots$O)	$\angle\alpha$	$\angle$(HOH)	$\angle\beta$	Ref.
r_e(H$_2$O) [a]	0.9578				104.50		46
r_e(HF) [a]		0.9168					47
MP2/6-311++G(2d,2p)	0.959	0.934	2.663	2.1	105.24	130.5	48
MP2/AVQZ			2.652	1.4		132.6	11
r_0 [b]			2.676(3)			143.2(35)	9
r_m [c]			2.6593(7)			131.05(44)	9
r_e [a]	0.9579	0.9324	2.6485	1.61	105.62	132.67	pi [d]

[a] Equilibrium structure.
[b] Empirical effective structure.
[c] Empirical mass-dependent structure.
[d] pi = present investigation.

Table 5. DFT structures for $H_2O\cdots HF$ (distances in Å and angles in degrees).

| Method	basis set [a]	r(OH)	r(HF)	r(F$\cdots$O)	$\angle\alpha$	$\angle$(HOH)	$\angle\beta$	r(O$\cdots$H)
B3LYP	AVTZ no CP	0.9628	0.9450	2.6366	1.618	106.112	130.767	1.6922
B3LYP	AVTZ	0.9628	0.9448	2.6385	1.609	106.121	131.008	1.6943
B3LYP	apc3	0.9614	0.9423	2.6400	1.598	106.158	131.488	1.6983
B3LYP	6-311+G(3df,2pd)	0.9618	0.9419	2.6454	1.686	106.103	131.873	1.7041
PW91	6-311+G(3df,2pd)	0.9692	0.9548	2.6211	2.028	105.327	124.676	1.6672
BMK	6-311+G(3df,2pd)	0.9582	0.9356	2.6517	1.904	106.672	135.661	1.7169
B97-1	6-311+G(3df,2pd)	0.9606	0.9385	2.6512	1.922	105.724	129.942	1.7135
B97-1	apc2	0.9608	0.9397	2.6456	1.800	105.795	129.723	1.7066
B97-1	apc3	0.9605	0.9391	2.6452	1.819	105.773	129.516	1.7068
B97-1	AVTZ	0.9617	0.9415	2.6433	1.789	105.743	129.185	1.7025
BLYP	acp2	0.9721	0.9563	2.6622	1.634	105.492	127.416	1.7065

[a] With CP correction unless otherwise stated.
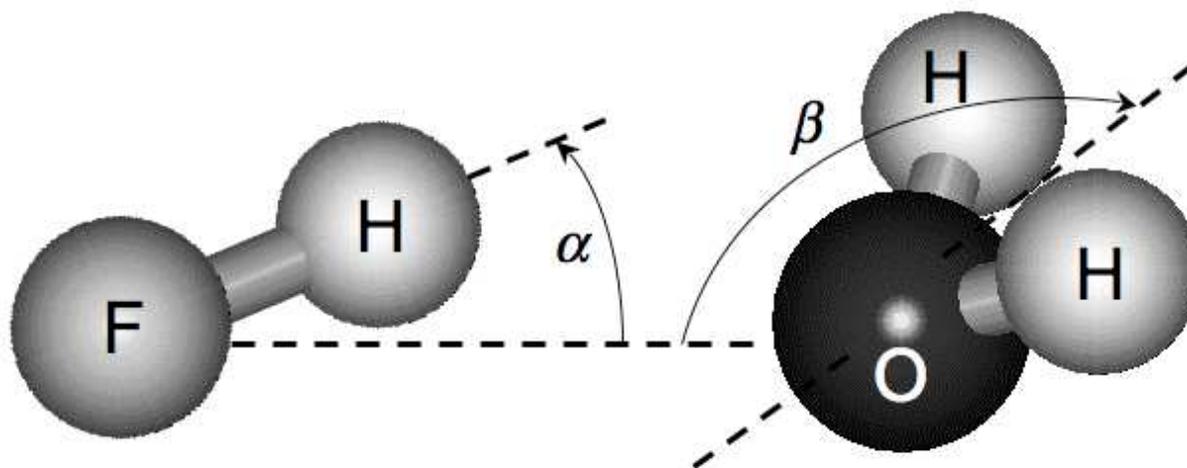
Figure 1. Equilibrium geometrical structure of H_2O-HF. Parameter β is the angle between the F-O direction and the bisectrix of the HOH angle. Parameter α corresponding to the OFH angle characterizes non- linearity of the F-H-O skeleton. This angle is not visible on the Figure because of its small value (< 2 degrees).

Figure 2. Plot of the $r(O \cdots H)$ and $r(O \cdots F)$ bond lengths (in Å) as a function of the cardinal number n of the AVnZ basis set.
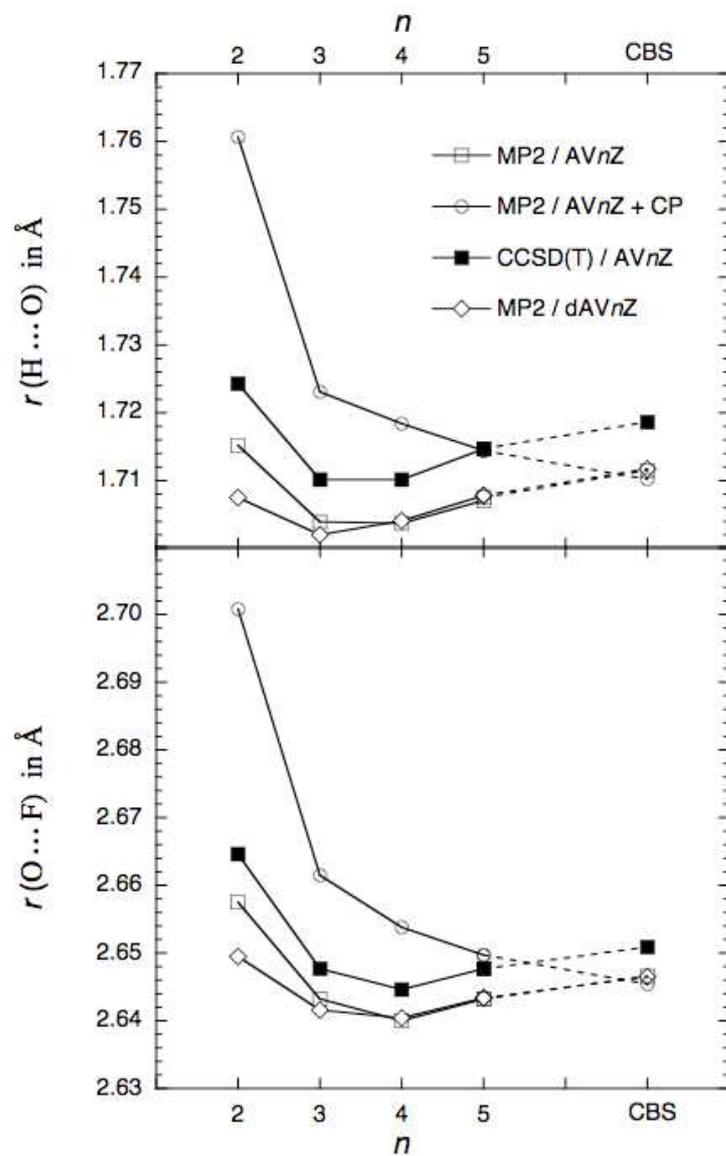
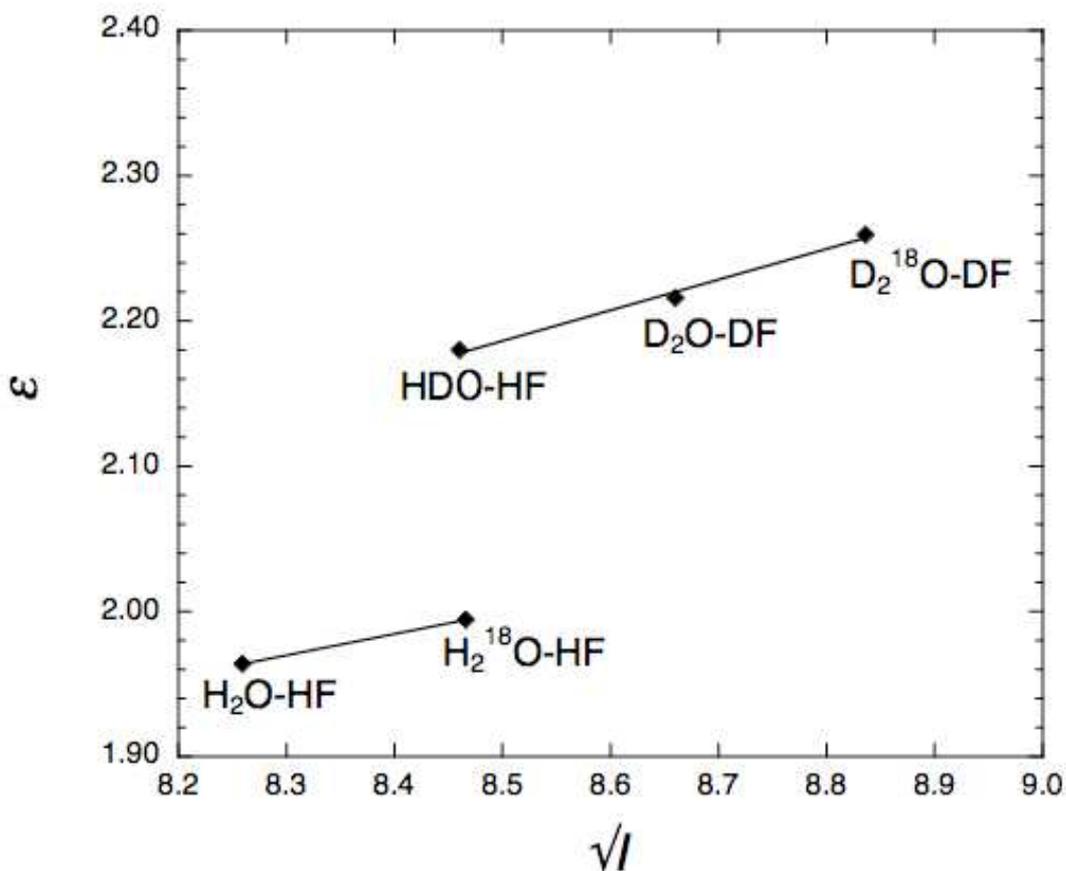Figure 3. Plot of ε as a function of $\sqrt{I}$ for the different isotopologues of $H_2O\cdots HF$ (with

$I = h^2/4\pi^2(B+C)$; ε and I in $u\text{Å}^2$)

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