

***Ab initio* MP2 study of the HF ... ClF complex using various extended basis sets and bond functions**

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Summary. The stationary points on the intermolecular potential energy surface (PES) for the HF...ClF complex have been investigated at the second-order Møller–Plesset perturbation theory (MP2) level using various extended basis sets, including diffuse functions, and also bond functions. The last ones were placed at different intermolecular positions, for distinct stationary points. The basis set superposition errors (BSSE) were accounted for using the counterpoise method. Besides the anti-H-bonded and H-bonded minimum energy structures, four transition state structures were also located on the PES. It was shown that higher polarization functions are required for the description of the anti H-bonded isomer and diffuse functions had to be included for the H-bonded isomer. The bond functions are able to replace the $f(\text{Cl, F})$ and $d(\text{H})$ polarization functions at a lower computational cost. However, for the H-bonded isomer intramolecular electron correlation also plays an important role. So we have to use diffuse nucleus centered polarization functions for an adequate description of intermolecular and intramolecular correlation.

Key words: van der Waals complex – Transition states – Extended basis sets – Bond functions – Electronic correlation

1 Introduction

The study of weakly bound molecular complexes has been an intensive research field in the last years at theoretical [1–5] and experimental levels [6–9]. *Ab initio* calculations have shown to be a powerful tool for the study of these complexes, through the analysis of structural aspects and stability [10–13], the calculation of the potential energy surface (PES) for posterior determination of the rovibrational spectrum [14], tunneling splitting [15, 16] and the determination of thermodynamics properties in the gas phase [17, 18].

The quality of the *ab initio* calculations depends mainly on the basis set utilized, and the electronic correlation should be included, at least, until second order, like second-order Møller–Plesset perturbation theory (MP2), coupled electron pair approximation (CEPA), coupled pair functional (CPF) method, etc. For more accurate calculations, it would be necessary to include several and higher order

polarization functions, and highly diffuse *sp* functions. For a good performance, the exponents should be carefully chosen. The standard basis set with polarization functions is not the best option for the interaction energy calculation in complexes, because it is calibrated to give a lower absolute energy value. However, for the study of van der Waals complexes, the basis set functions should be able to give a good description of monomers physical properties, reproducing multipolar moments and polarizabilities of each molecule. This can be obtained using the standard basis set augmented with polarization functions with suitable optimized exponents [1, 3]. Nevertheless, the use of higher order polarization functions (*f* for the second row atoms and *d* for H) can be substituted for bond functions, placed at the van der Waals bond [19–22], which reduces the computational costs.

The HF–ClF complex is a system with two minimum energy structures on the intermolecular PES, corresponding to the isomeric H-bonded and anti H-bonded forms. In the first case, the HF molecule is the Lewis acid, where the H atom is bonded to the F atom of the ClF subunit. In the anti H-bonded structure, the ClF is the acid, and the van der Waals bond is between the F and Cl atoms. An experimental study [23] lead to the conclusion that the anti H-bonded structure is the more stable, with the F, Cl and F atoms in line, and the H atom at a 55° angle of this line. The intermolecular distance between the Cl and F atoms was estimated as 2.76 Å.

A posterior theoretical study was done by Hobza and co-workers [24], where the 4-31 G* basis set was utilized. They found that the H-bonded species was slightly more stable than the anti-H-bonded one. Some years latter, Rendell et al. [25] reported an *ab initio* study with a TZP basis set, including electronic correlation at the (CPF) level. Neglecting the correction for the basis set superposition error (BSSE) as in the work of Hobza et al. [24] resulted that the H-bonded structure was more stable by 119 cm⁻¹. However, the inclusion of BSSE correction lead to the anti-H-bonded species to be more stable by 27 cm⁻¹, and the zero point energy (ZPE) contribution increased this stability to 209 cm⁻¹.

More recently, De Almeida et al. [26, 27] carried out a detailed analysis of the intermolecular PES for this complex, at the HF/4-31G, MP2/6-31 + G** and MP2/6-311G** levels. They located five different stationary points on the multi-dimensional PES, the two minima described before (anti-H-bonded and H-bonded), two second order transition states (TS) corresponding to midway between equal structures of the two minima, and a first order TS connecting the two isomers. However, this calculation were not BSSE corrected. So, a properly BSSE treatment is necessary.

In this work, we have analyzed the intermolecular PES for the HF–ClF dimer at the DZP (double zeta plus polarization function) level, with the previous known stationary points being located. Then, we have expanded the basis set, including more polarization functions, highly diffuse *sp* functions and bond functions and included the electronic correlation at the MP2 level. The methodology of calculation is in section 2. The results are presented and discussed in section 3 and the conclusions are in section 4.

2 Calculations

The minimum energy and TS structures located on the PES for the HF–ClF complex were fully optimized with the standard DZP [28] basis set, that correspond to contraction (11s7p/6s4p) for Cl, (9s5p/3s2p) for F and (3s/2s) for H,

Table 1. Description of the ten different basis set used for the calculation of the energy of the stationary points on the PES for the HF-ClF complex

Basis set number	Basis set Cl/F/H	Polarization exponents
1	DZ + [1d/1d/1p] ^a	0.75/0.9/1.0
2	DZ + [2d/2d/2p]	0.5, 0.22/1.0, 0.36/1.0, 0.2
3	DZ + [2d1f/2d1f/2p1d]	0.5, 0.2, 0.17/1.0, 0.36, 0.275/1.0, 0.2, 0.75
4	DZ + [2d/2d/2p] + {2s2p} ^b	0.5, 0.22/1.0, 0.36/1.0, 0.2
5	DZ + [2d/2d/2p] + diff ^c	0.5, 0.22/1.0, 0.36/1.0, 0.2
6	DZ + [2d/2d/2p] + diff + {2s2p}	0.5, 0.22/1.0, 0.36/1.0, 0.2
7	DZ + [2d/2d/2p] + [1f/1d] ^d	0.5, 0.22/1.0, 0.36/1.0, 0.2 + 0.275/0.075
8	DZ + [2d/2d/2p] + diff + [1d1f/1p1d] ^e	0.5, 0.22/1.0, 0.36/1.0, 0.2 + 0.1076, 0.275/0.036, 0.075
9	DZ + [2d/2d/2p] + 2{2s2p} ^f	0.5, 0.22/1.0, 0.36/1.0, 0.2
10	DZ + [2d/2d/2p] + diff + 2{2s2p}	0.5, 0.22/1.0, 0.36/1.0, 0.2

^a This corresponds to DZP standard basis set

^b Bond functions placed at midway of the van der Waals bond with exponents 0.5, 0.2, 0.5, 0.2

^c This corresponds to standard diffuse *s* functions on H atom and *sp* diffuse on other atoms

^d This corresponds to *f* function on F atom and *d* function on H atom in the H-bond isomer

^e The same as *d*, but added highly diffuse *d* and *p* functions on F and H respectively

^f Two bond functions, one midway of H-F intermolecular bond and other on midway of F-Cl intermolecular bond

augmented with *d* functions for Cl and F, and *p* functions for H with exponents 0.75, 0.9 and 1.0 respectively.

After the geometry optimizations, we had progressively augmented the basis set, including electronic correlation at the MP2 level and BSSE correction by the counterpoise method [29]. The ten different basis set used are described in Table 1, with the respective exponents of the polarization functions. The diffuses *s*(*H*) and *sp*(F, Cl) functions used have exponents 0.036, 0.1076 and 0.0483 respectively. The set of bond functions {2s2p} have exponents 0.5, 0.2, 0.5, 0.2. All calculations were performed with the GAMESS package [30] at the Laboratório de Química Computacional e Modelagem Molecular (LQC-MM) of the Departamento de Química, UFMG.

3 Results and discussions

The optimized structures can be found in Fig. 1. The structures I (anti-H-bonded) and III (H-bonded) correspond to minima, II and IV stand for second-order TS, structure V is a first order TS and the structure VI is a third order transition state. Except for VI, all other structures were reported by De Almeida et al. [26].

Table 2 shows our results for the geometric parameters of several structures, like those defined in Fig. 1, together with the results of De Almeida et al. [26], Rendell et al. [25] and Novick et al. [23]. Our optimizations at the Hartree Fock self-consistent field (SCF) level show a shorter intermolecular length, and a longer van der Waals bond length than the MP2 and CPF optimizations. The bond angles showed a better agreement. Only structure V presents a more accentuated deviation. Nevertheless, we believe these small differences will not affect substantially our results.

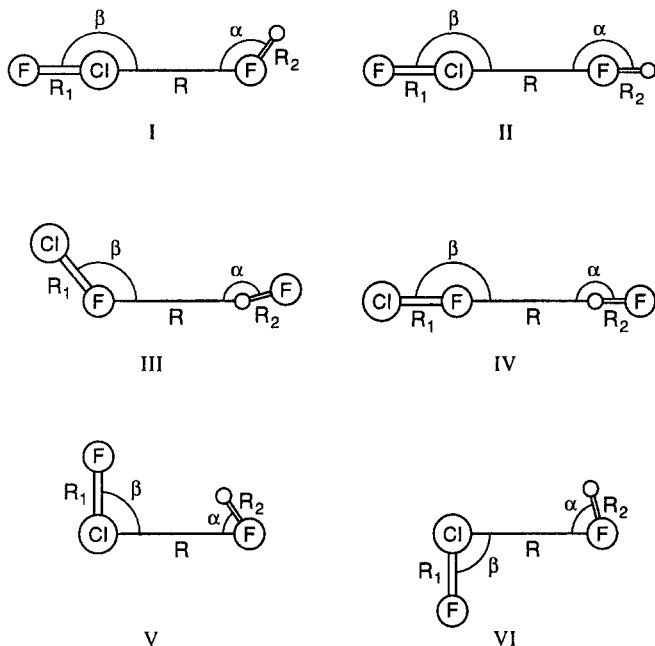


Fig. 1. The fully optimized (SCF/DZP) stationary points on the PES for the HF-ClF complex: I – Anti H-bonded isomer; II – second order transition structure; III – H-bonded isomer; IV – second order transition structure; V – first order transition structure; VI – third order transition structure

In order to analyze the stability of each stationary point, we define D_e as the difference between the complex and monomers total energies, corrected for BSSE. Also, we have decomposed the D_e values into SCF and electronic correlation components, in order to analyze each contribution ($D_{e_{SCF}}$ and $D_{e_{COR}}$).

The results for the minimum energy structure I and the transition state II can be found in Table 3, where h is the energy difference between I and II ($h = D_{e_I} - D_{e_{II}}$). The standard DZP basis set produces a D_e of 753 cm^{-1} and a h value of 86 cm^{-1} . The use of two polarization functions (basis set 2) causes a little decrease in D_e (to 719 cm^{-1}) and increase h to 114 cm^{-1} . However, in observing the SCF and correlation components, notable variations are observed. The value of $D_{e_{SCF}}$ falls from 718 to 550 cm^{-1} , while $D_{e_{COR}}$ increases from 35 to 169 cm^{-1} . The small net variation of D_e is due to canceling of errors. Adding higher polarization functions (basis set 3) also leads to a decrease in $D_{e_{SCF}}$ to 530 cm^{-1} and increases $D_{e_{COR}}$ to 233 cm^{-1} , resulting in a final D_e of 763 cm^{-1} , near of 753 cm^{-1} found with the DZP basis set. However, h increases to 133 cm^{-1} , comparing with 86 cm^{-1} of the DZP calculations. The addition of bound functions to basis set 2 (basis set 4) leads to a result near of the basis set 3 ones. The effect of sp diffuse functions (basis set 5) is small, resulting in light differences of basis set 2, and the inclusion of bond functions (basis set 6) leads to results close to the basis set 3 ones. Naturally, basis set 3 and 6 correspond to the best results. The correlation energy ($D_{e_{COR}}$) of basis set 3 is 10 cm^{-1} larger than the value found with basis set 6, and so the first basis set describes better the dispersion contribution for the interaction energy. Therefore, basis set 3 gives a slightly better result for this isomer than basis set 6.

The significant variation of SCF and electronic correlation contributions in going from basis set 1 to 2 can be attributed to a better description of polarizabilities of the monomers obtained by the inclusion of more diffuses d and p functions,

Table 2. Comparison of the results of different works for geometric parameters of the stationary points structures of the HF ... CIF complex

Structure	Work	R	R ₁	R ₂	α	β
I	Present ^a	2.82	1.61	0.90	126	177
	De Almeida ^b	2.74	1.67	0.93	126	179
	Rendell ^c	2.76	1.63	0.92	118	177
	Expt. ^d	2.76	—	—	125	180
II	Present ^a	2.87	1.61	0.90	180	180
	De Almeida ^b	2.82	1.67	0.93	180	180
III	Present ^a	2.04	1.61	0.90	171	130
	De Almeida ^b	1.93	1.68	0.93	173	118
	Rendell ^c	1.93	1.63	0.92	170	115
IV	Present ^a	2.09	1.61	0.90	180	180
	De Almeida ^b	2.09	1.67	0.93	180	180
V	Present ^a	3.71	1.61	0.90	58	93
	De Almeida ^b	3.53	1.67	0.93	14	115
VI	Present ^a	4.19	1.60	0.90	79	78

^a This study at the SCF/DZP level^b Ab initio MP2/6-31 + G** results from Ref. [26]^c Ab initio CPF/TZP results from Ref. [25]^d Experimental microwave spectroscopy results from Ref. [23]**Table 3.** Stabilization energies (De, in cm⁻¹), calculated using different basis sets, of anti-H-bonded isomer and barrier heights (h, in cm⁻¹) to go from minimum structure I to an equivalent configuration via the transition state II. All calculations were BSSE corrected

Basis set	De _{SCF} ^a	De _{COR} ^b	De	h _{SCF} ^a	h _{COR} ^b	h
1	718	35	753	48	38	86
2	550	169	719	57	57	114
3	530	233	763	65	68	133
4	532	214	746	52	67	119
5	542	181	723	65	62	127
6	525	223	748	55	70	125

^a SCF contribution^b Electronic correlation contribution

which permits obtain a more realistic induction (SCF term) and dispersion (electronic correlation term) interaction energies in the complex.

Our results for the H-bonded species (minimum energy structure III and transition state IV) are shown in the Table 4. Again, *h* represents the energy barrier to go from the minimum energy structure II to an equivalent configuration through the TS structure IV. The basis set 2 produces a De_{SCF} of 568 cm⁻¹, and a De_{COR} of 42 cm⁻¹, and so the electronic correlation contributes with just 7% of De. Including higher polarization functions (basis set 3) increases De_{SCF} to 603 cm⁻¹ but leaves De_{COR} practically unaltered. The final value of De increases to

Table 4. Stabilization energies (D_e , in cm^{-1}), calculated using different basis sets, of H-bonded isomer and barrier heights (h , in cm^{-1}) to go from minimum structure III to an equivalent configuration via the transition state IV. All calculations were BSSE corrected

Basis set	$D_{e_{\text{SCF}}}^a$	$D_{e_{\text{COR}}}^b$	D_e	h_{SCF}^a	h_{COR}^b	h
2	568	42	610	187	104	291
3	603	44	647	160	108	268
4	576	75	652	156	109	265
5	511	24	535	176	105	281
6	529	58	587	153	110	263
7	603	54	657	151	106	257
8	532	34	566	143	107	250

^a SCF contribution

^b Electronic correlation contribution

647 cm^{-1} and h falls to 268 cm^{-1} . The inclusion of bond function (basis set 4) has a small effect on $D_{e_{\text{SCF}}}$, but it increases substantially $D_{e_{\text{COR}}}$ to 75 cm^{-1} . This difference in relation to basis set 3 can be attributed to the influence of the intramolecular correlation, which is not taken into account by the bond functions. The intramolecular correlation is repulsive, and can be obtained using nucleus centered basis set, or bond functions placed on the monomers. The diffuse functions play a very important role in the description of H-bonded complex. Their inclusion (basis set 5) decreases $D_{e_{\text{COR}}}$ by 18 cm^{-1} , confirming the suspicion of the importance of intramolecular correlation. A more important effect is obtained in the $D_{e_{\text{SCF}}}$ contribution. It is decreased by 57 cm^{-1} , resulting a total fall of 75 cm^{-1} in D_e , which goes to 535 cm^{-1} . The basis sets 6, which is built by adding bond functions to the basis set 5, produces a $D_{e_{\text{COR}}}$ value which is not adequate because of the presence of intramolecular correlation. For an adequate use of bond functions, it would be necessary first to saturate the intramolecular correlation. Basis set 7 results of the addition to basis set 2 of d functions on H atoms and f functions on F atoms of the H-bonded species. The value of $D_{e_{\text{SCF}}}$ is identical to the basis set 3, while D_e is 10 cm^{-1} greater. The functions placed near of the van der Waals bond favor the intermolecular correlation. A more adequate basis set would be basis set 7 augmented with sp diffuse functions. Basis set 8, beyond sp diffuses, have highly diffuses polarization d and p functions. Of all basis sets, this describes better the complex, resulting in a D_e value of 566 and 250 cm^{-1} for the barrier height. The energy barriers calculated with other basis sets are near to this value, the results of the basis sets 2 exhibiting the largest deviation, with a h value of 291 cm^{-1} . The variation of h_{COR} , in special, is not significant.

The calculations for the first order TS (structure V) are in Table 5. The D_e value evaluated with basis set 2 is 167 cm^{-1} , with $D_{e_{\text{SCF}}}$ of 88 cm^{-1} and $D_{e_{\text{COR}}}$ of 79 cm^{-1} . So, the interaction energy for this species has a great contribution of the electronic correlation term. The addition of diffuse function in basis set 2 (basis set 4) leads to a large effect in $D_{e_{\text{SCF}}}$, lowering this term by 23 cm^{-1} , and increasing $D_{e_{\text{COR}}}$ by 7 cm^{-1} , while higher polarization functions (basis set 3) cause a larger effect in $D_{e_{\text{COR}}}$ (increased by 23 cm^{-1}) and decreases $D_{e_{\text{SCF}}}$ by 8 cm^{-1} . Both types of functions are necessary to obtain a good description of this structure. Basis set 9 is formed by the addition of two bond functions to basis set 2. Its effect should be in the same direction of the basis set 3. Indeed, $D_{e_{\text{SCF}}}$ is near of basis set 3 results

Table 5. Stabilization energies (De, in cm^{-1}) for structure V for several basis sets. All calculations were BSSE corrected

Basis set	$\text{De}_{\text{SCF}}^{\text{a}}$	$\text{De}_{\text{COR}}^{\text{b}}$	De
2	88	79	167
3	80	102	182
5	65	86	151
9	77	116	193
10	55	115	170

^a SCF contribution^b Electronic correlation contribution**Table 6.** Stabilization energies (De, in cm^{-1}) for structure V. All calculations were BSSE corrected

Basis set	$\text{De}_{\text{SCF}}^{\text{a}}$	$\text{De}_{\text{COR}}^{\text{b}}$	De
6	-84	78	-6

^a SCF contribution^b Electronic correlation contribution

(77 cm^{-1} compared to 80 cm^{-1}), but the correlation contribution is larger (116 cm^{-1} compared to 102 cm^{-1}). The inclusion of diffuse functions in basis set 9 (basis set 10) have almost no changes in De_{COR} (115 cm^{-1} compared to 116 cm^{-1}). This result indicates that De_{COR} is saturated at the intramolecular and intermolecular levels. The contribution of De_{SCF} falls 22 cm^{-1} , practically the same variation of basis set 2 to basis set 5 (23 cm^{-1}). The final value of De (basis set 10) is 170 cm^{-1} , and represents our best value for this geometry.

Structure VI was calculated only with basis set 6 and leads to a nonbonding structure with De of -6 cm^{-1} , although it is bonded when BSSE is not considered. The results are given in the Table 6.

According with the facts observed above, the inclusion of several polarization functions is crucial for the description of anti-H-bonded isomer, due to its effect in the SCF contribution and in the electronic correlation contribution. The diffuse functions are of small importance. For the best basis set (basis set 3), the correlation energy contributes with 30% of De value, while the DZP basis set just do 5%. So, the previous calculation with smaller basis set could not lead to precise results, inasmuch as fortuitous errors cancel. Table 7 shows our best values, and compares it with the ones obtained in Refs. [25, 26]. De Almeida et al. have not included BSSE correction in their calculations, and as a consequence the reported De value is very high, however the h value is in reasonable agreement with the present study. The De_{SCF} and De_{COR} values of Rendell et al. are very different from the results presented here, although De is in reasonable concordance. It happens because they have just used one polarization function. If we compare it with our DZP values, the contributions are close. So, their good value of De is due to errors canceling.

For the H-bonded complex, Rendell et al. obtained De_{SCF} very high because they did not introduce *sp* diffuse functions. The correlation contribution is small

Table 7. Comparison of the stabilization energies for the stationary points located on the PES for the HF–ClF complex between our best results and the results available in the literature. h stands for the height barrier for tunneling motion through a linear transition state structure

Structure	Work	De _{SCF} ^a	De _{COR} ^b	De	h
I (anti-H-bonded)	Present ^c	530	233	763	133
	De Almeida ^d	—	—	1027	111
	Rendell ^e	703	24	727	—
I (H-bonded)	Present ^f	532	34	566	250
	De Almeida ^d	—	—	1106	437
	Rendell ^e	665	35	700	—
V	Present ^g	55	115	170	—
	De Almeida ^d	—	—	190	—
VI	Present ^h	– 84	78	– 6	—

^a SCF contribution

^b Electronic correlation contribution

^c This study at MP2/(basis set 3)//SCF/DZP (BSSE corrected)

^d *Ab initio* MP2/6-31 + G** results from Ref. [26]

^e *Ab initio* CPF/TZP (BSSE corrected) results from Ref. [25]

^f This study at MP2/(basis set 8)//SCF/DZP (BSSE corrected)

^g This study at MP2/(basis set 10)//SCF/DZP (BSSE corrected)

^h This study at MP2/(basis set 6)//SCF/DZP (BSSE corrected)

(6% of De in the basis set 8) and their value is near to ours (35 cm⁻¹ compared to 34 cm⁻¹). In consequence, their final energy is 134 cm⁻¹ higher than our best value. So, our calculations predict a stability of 197 cm⁻¹ for the anti-H-bonded in relation to the H-bonded one, against 27 cm⁻¹ of Rendell et al. (no ZPE included). De Almeida et al. obtained a larger stabilization energy for the H-bonded (79 cm⁻¹), because they have not done correction for BSSE. In doing BSSE correction, the H-bonded species undertake a larger variation, because in this isomer the bond length is smaller, and each monomer uses more the basis functions of the other. For the structure V, the monomers are more distant, and the BSSE decreases. It may justify the good concordance of the result of De Almeida et al. (190 cm⁻¹) and the present one (170 cm⁻¹). However, we should remember that this structure have different geometric parameters comparing with the data of De Almeida et al.

For a better analysis of the complex stability, we should add the zero point energy ZPE. So, we used the harmonic frequencies calculated by De Almeida et al. [26] (MP2/6-31 + G**) to produce the ZPE value of 238 cm⁻¹ for the anti-H-bonded and 435 cm⁻¹ for H-bonded. Our calculated stabilization energies of the species anti- and H-bonded are in Table 8. Our results lead to a considerable stabilization of the anti-isomer in relation to the H-bonded one. The value given by Rendell et al. is smaller because they do not include more polarization functions, and specially diffuse functions in the H-bonded complex. The results derived by De Almeida et al. are not corrected for BSSE, which result in a smaller stabilization of anti-H-bonded. Our results are in agreement with the experimental study [23] where only the anti-isomer was observed.

Table 8. Comparison between stabilization energies with zero point energy correction for structures I and III calculated in different works

Work	D_0 (I)	D_0 (III)	D_0 (I) – D_0 (III)
Present ^a	525	131	394
De Almeida ^b	789	671	118
Rendell ^c	500	290	210

^a This study at MP2/(basis set 3)//SCF/DZP (BSSE corrected) for D_0 (I) and MP2/(basis set 8)//SCF/DZP (BSSE corrected) for D_0 (III). The ZPE contribution was obtained at MP2/6-31 + G** level taken from Ref. [26]

^b *Ab initio* MP2/6-31 + G** results from Ref. [26]

^c *Ab initio* CPF/TZP (BSSE corrected) results from Ref. [25]

The possibility of tunneling in the two isomers, where the minimum (I and III) pass through the transition state (II and IV) was suggested by De Almeida et al. [26]. The species anti-H-bonded has a interconversion barrier of 133 cm^{-1} , and practically only the H atom can move. The bending mode of 78 cm^{-1} , calculated by De Almeida et al. [27] should correspond to the vibration along the tunneling coordinate, and is possible to have two doublets down the barrier, which could be detected in the experimental measurements. The H-bonded species has a interconversion barrier of 250 cm^{-1} , and the motion is mainly due to the Cl atom. Due its larger mass, and barrier height, the tunneling is very unlikely to take place in this case. A study in this direction is in progress [31].

4 Conclusion

We performed *ab initio* calculations on the HF ... CIF complex, locating the stationary points at the SCF/DZP level and using an augmented basis set and MP2 correlation level to obtain an accurate determination of stabilization energies for several structures. We show the need for utilizing higher polarization functions in the study of HF ... CIF complex, and also the necessity of including diffuse functions in the H-bonded isomer. Bond functions were used, and we show that it can replace the $f(\text{Cl}, \text{F})$, $d(\text{H})$ polarization functions, with exception of structures III and IV (H-bonded), where the intramolecular correlation is important. Adding zero point energy correction to the calculated dissociation energies (De), we obtained that the anti-H-bonded isomer is more stable than the H-bonded by ca. 394 cm^{-1} , in agreement with the experimental study where only the anti-isomer was observed.

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