Basis set effects in the description of the Cl-O bond in ClO and XClO isomers (X=H,O,Cl) using DFT and CCSD(T) methods

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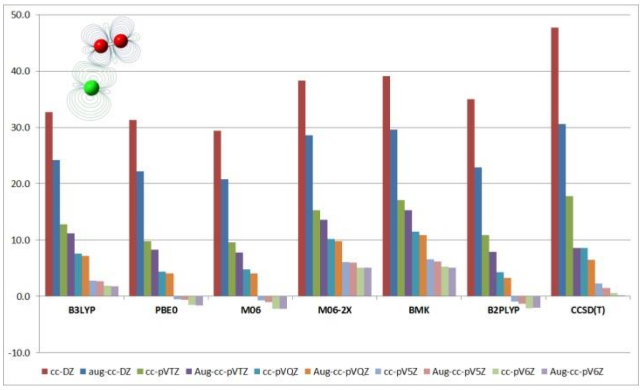
Graphical abstract



Abstract

The performance of a group of density functional methods of progressive complexity for the description of the ClO bond in a series of chlorine oxides was investigated. The simplest ClO radical species as well as the two isomeric structures XClO/ClOX for each X=H, Cl and O were studied using the PW91, TPSS, B3LYP, PBE0, M06, M06-2X, BMK and B2PLYP functionals. Geometry optimizations as well as reaction enthalpies and enthalpies of formation for each species were calculated using Pople basis sets and the (aug)-cc-pVnZ Dunning sets, with n=2-6. For the calculation of enthalpies of formation, atomization as well as isodesmic reactions were employed. Both the precision of the methods with respect to the increase of the basis sets, as well as their accuracy, were gauged by comparing the results with the more accurate CCSD(T) calculations, performed using the same basis sets as for the DFT methods. The results obtained employing composite chemical methods (G4, CBS-QB3 and W1BD) were also used for the comparisons, as well as the experimental results when they are available. The results obtained show that error compensation is the key for successful description of molecular properties (geometries and energies) by carefully selecting method and basis sets. In general, expansion of the one-electron basis set to the limit of completeness does not improve results at the DFT level, but just the opposite. The enthalpies of formation calculated at the CCSD(T)/aug-cc-pV6Z for the species considered are generally in agreement with experimental determinations, and the most accurate derived theoretically up to present. Different sources of error in the calculations are discussed in detail.

Keywords

density functional methods; enthalpy of formation; basis sets convergence; chlorine oxides

Introduction

Ozone loss over the Antartic was reported by Farman *et al* in 1985 [1]. Several hypotheses were proposed to explain the Antarctic ozone hole, of which the ones obtaining the largest success were those related to halogen catalyzed ozone loss [2] [3] [4]. Ground-based measurements of ClO, HCl, ClONO2, and OClO obtained in Antarctica during 1986 indicated that ozone depletion is associated with elevated abundances of ClO. A plethora of research on the behavior of chlorine and bromine compounds in the atmosphere was then started.

It is known today that stratospheric ozone is largely destroyed by radical reactions involving XO radicals (X=H, Cl or Br). Self-reaction of these radicals, with the same or different X, give rise to XYO_2 species (with Y also H, Cl or Br) of which two of the most interesting are $HClO_2$ and Cl_2O_2 [5]. These species exhibit a similar behavior, with several possible stable isomers. Many theoretical studies have been performed, but it is not absolutely clear whether the more stable isomer computed is actually the observed one. For instance, it is well known that chlorous acid has the structure HOClO, at least in solution. However, the most stable isomer in gas phase seems to be the HOOCl peroxide. In the case of Cl_2O_2 instead, the most stable isomer seems to be $ClClO_2$ instead of the peroxidic structure.

Theoretical studies aim fundamentally to the determination of thermochemical and kinetic data, which are essential for building models of the catalytic cycles. Calculating accurate data, which rival the experimental determinations when these latter are known, is not a trivial matter. Geometries, spectroscopic properties and energetic information obtained depend heavily on the theoretical methods employed and the one-electron basis sets used within them. In relation to the subject of enthalpies of formation, central to the formulation of atmospheric kinetic models, recent papers by Somers and Simmie [6] and by Rogers et al [7] discuss some of the complexities associated to these studies.

In the case of compound methods, accuracy is aimed at through addition of energies obtained at different levels and with different basis sets [7]. In the case of direct calculations, high level molecular orbital methods (CCSD(T) usually) or density functional methods (DFT) are combined with isogiryc or isodesmic reactions [8] [9].

It is well known that molecular orbital methods do depend heavily on the basis set chosen. It is less commonly recognized that this is also true in certain cases for DFT methods. In this work we have performed a careful investigation of the effects of methods and basis sets on the description of the ClO bond in ClO and XClO (X=H,O,Cl) species, using molecular orbital methods (MP2, CCSD(T)), chemical models (CBS-QB3, G4 and W1BD) and DFT methods representing different rungs of the Jacob´s ladder (PW91PW, TPSS, B3LYP, PBE0, M06, M06-2X, BMK and B2PLYP) [10] [11]. Our purpose is to investigate the performance of DFT methods with respect to molecular orbital ones, as well as their rate of convergence with increasingly extended basis sets. To this end we have used Pople´s basis sets and Dunning´s correlation consistent basis sets from cc-pVDZ to aug-cc-pV6Z.

Results are reported for geometries, IR spectra and energies of ClO, XClO and XOCl, where X= H, O or Cl. Whenever possible, the theoretical results have been compared with the experimental ones. In cases when these results are not available, a rational guess of the estimated values with their expected error bars is provided.

Methods

Geometry optimization and calculation of the energies were performed at the molecular orbital and DFT levels. MP2, CCSD(T) [12] [13] and composite models CBS-QB3 [14], G4 [15] and W1BD [16] were employed on the molecular orbital side. On the DFT side, methods belonging to different rungs in the Jacob´s ladder [17] were used. The methods chosen were the GGA PW91 [18] (for both exchange and correlation), the meta GGA TPSS [19], the hybrid GGAs PBE0 [20] and B3LYP [21], the hybrid meta GGAs M06 [22], M06-2X [22] and BMK [23], and the double hybrid B2-PLYP [24].

Two Pople basis sets, 6-31+G(d,p) and 6-311++G(2df,2pd), were chosen as representative of those commonly employed in theoretical chemistry calculations. Convergence of different properties were investigated using Dunning´s cc-pVnZ and aug-cc-pVnZ, with n from 2 to 6 (which includes up to *i* functions on the chlorine atom), see refs. [25], [26] and references therein.

Geometry optimization of all the species was fully performed for each and all models (method/basis set combination). Forces were reduced until a precision of at least 10^{-4} Å was obtained in the Cartesian coordinates. Thermochemical properties were obtained within the harmonic oscillator/rigid rotor model. Analytical second derivatives were used whenever possible.

Calculations were performed using the Gaussian 09 set of computer programs [27] for the DFT and model chemistry calculations and the Molpro code [28] [29] for the post-Hartree-Fock calculations. A mixed cluster of Xeon and Opteron machines was employed for the calculations, with a maximum of 32 cores per job and 4GB per core.

Results and Discussion

ClO. This is the simplest chlorine oxide possible. The experimental bond length was determined in 1968 by Amano and coworkers [30] as 1.5696 Å and more recently by Drouin et al [31] as 1.569539 Å. The heat of formation at 298.15 K was measured experimentally as 24.29 ± 0.03 kcal/mol [32] while it is listed as 24.192 kcal/mol in the JANAF data tables [33]. Grant et al [33] calculated this enthalpy of formation as 24.9

kcal/mol using the R/UCCSD(T) method [12] [13]with the augmented correlation consistent basis sets aug-cc-pVnZ (n = D, T, Q, 5). The best theoretical value was reported by Karton et al [34], who obtained 24.19 ± 0.19 kcal/mol at 0 K and 24.18 ± 0.03 at 298 K using the W4 method (see ref. [35] and references therein).

In this paper we calculated the enthalpy of formation employing both the atomization reaction

$$\mathrm{ClO}(^2\Pi) \rightarrow \mathrm{Cl}(^2\mathrm{P}) + \mathrm{O}(^3\mathrm{P}) \tag{1}$$

and the reaction of formation from the diatomics

$$2\ \mathrm{ClO}(^2\Pi) \rightarrow \mathrm{Cl}_2(^1\Sigma_g^+) + \mathrm{O}_2(^3\Sigma_g^-) \tag{2}$$

The necessary experimental enthalpies of formation of the atoms in reaction (1) are $\Delta_f H_{gas}^0$(Cl) = 28.992 ± 0.002 kcal/mol and $\Delta_f H_{gas}^0$(O) = 59.555 ± 0.024 kcal/mol according to Cox et al [36]. The standard enthalpies of formation of the diatomics in reaction (2) are zero by definition.

Different degrees of error compensation are expected in the determination of the enthalpy of formation using reactions (1) and (2). Errors associated with the representation of the triplet state oxygen atom or molecule within each method/basis set model will not be compensated neither in reaction (1) nor in (2) since no other triplet species is present. However, reaction (1) does present a doublet species in the rhs and, therefore, would be expected to compensate for the errors associated to the description of the non-paired single electron in ClO. Neither of these reactions are homodesmic or isogyric so that error compentation is expected to be low. Moreover, to obtain a reasonably estimate of the bonding energy of ClO, which allows accurate calculation of the enthalpy of formation from reaction (1), one should include in the CCSD method full calculation of triples and perturbation estimation of quadruples (CCSDT(Q)), correct for core-correlation, introduce relativistic corrections and account for anharmonicity. This is clearly not the goal of this work, a task already performed by the application of W4 methods, but just the comparison between DFT and CCSD(T) methods to describe the ClO bond.

The calculated optimum bond length of ClO, as well as the enthalpies of reaction for reactions (1) and (2) are deployed in Table 1. Experimental results for the enthalpies of reaction, obtained from the experimental enthalpies of formation of the species involved, are listed in the last entry of the table. The calculated enthalpies of formation at 298.15K of ClO using the different models were obtained from the calculated enthalpies of reaction and the experimental enthalpies of formation of the species involved. These are also listed in the table, as well as the signed error with respect to the experimental result.

As we expected, the CCSD(T) values obtained with the large aug-cc-pV6Z are extremely accurate. The CCSD(T)/aug-cc-pV6Z model works well with for both reactions, but the enthalpy of reaction derived from reaction (1), 25.00 kcal/mol, is slightly worse than that derived from reaction (2), 24.91 kcal/mol. Some of the errors incurred are similar in both reactions (core correlation or lack of quadruple excitations for instance) while other are clearly different (spin orbit corrections for the atoms, for instance). All of these errors are either too small or compensate, so that the value obtained at the CCSD(T)/aug-cc-pV6Z level for the enthalpy of formation is only 0.7 kcal/mol above the experimental result.

Actually it can be shown that the error compensation of post-CCSD(T) contributions is larger. The addition of the complete triple, quadruple and quintuple excitations contributions to the TAE (Total Atomization Energy) plus the core correlation, relativistic and spin orbit contributions amount only to -0.01 kcal/mol (see Table 7 in ref. [35]). The TAE calculated at 0K in ref. [35] using the W4 method is 64.51 kcal/mol, while the one we obtain at the CCSD(T)/aug-cc-pV6Z level is 63.27 kcal/mol. The difference between these values is coming from two sources. On the one side, Karton et al do extrapolate to the CBS limit, while we are using only the values obtained at the aug-cc-pV6Z level. However, as can be seen in their Table 4, the different energies are already converged below 0.10 kcal/mol when th 5Z basis set is used. This fact is also supported by the difference we observed in the TAE between the results using the cc-pV6Z and aug-cc-pV6Z basis sets, only 0.23 kcal/mol. There is a higher probability that the difference is coming from the slightly erroneous geometry at which the calculations to obtain the W4 results were performed. The geometry optimization done by Karton and coworkers was at the CCSD(T)/cc-pV(Q+d)Z level only and the ClO bond length 1.575 Å is larger than the 1.5695 Å experimental value. Our own result, at the CCSD(T)/aug-cc-PV6Z level is 1.5694 Å. This is an error unaccounted for in the W4 calculations.

In passing, let it be said that the results obtained with CCSD(T) using Pople`s basis sets are far off the mark and very unreliable.

The three chemical models used, CBS-QB3, G4 and W1BD, are mucho more accurate than the MP2/6-311++G(2df,2pd) or CCSD(T)/6-311++G(2df,2pd) models for the calculation of the enthalpies of formation. The W1BD calculation is in fact even more accurate than the CCSD(T)/aug-cc-pV6Z result, at a fraction of the cost. In this particular case W1BD outperforms G4, contrary to the more general situation reported by Somers [6]. The optimum geometries in each case are not so good, but the ad hoc corrections to the energies actually improve very much the accuracy of the derived enthalpy of formation.

The DFT methods perform somehow erratically. The B2PLYP/6-311++G(2df,2pd) model, for instance, performs worse than the M06/6-311++G(2df,2pd) model, notwithstanding that the former procedure should be better and is considerably more costly. This observation notwithstanding, all the DFT results obtained using reaction (2) are extremely good even using Pople basis sets. The largest error was observed for M06-2X and was only 2.4 kcal/mol. For the TAE the results are similar, except that in this case neither the PW91 or TPSS methods with any basis set nor the other DFT methods with the smaller basis set, give good results. It can be observed that the DFT method may or may not improve with the increase of the basis set, an aspect we will discuss further in the following.

Table 1. Enthalpy of reaction for reactions (1) and (2) and enthalpy of formation of ClO derived from these reactions using different models (in kcal/mol); ClO bond length (in Å)

Method	Basis set	Cl+O → ClO			$Cl_2+O_2 \rightarrow 2ClO$			Bond length	
		$\Delta H_r^0(298K)$	$\Delta H_f^0(298K)$	δ^a	$\Delta H_r^0(298K)$	$\Delta H_f^0(298K)$	δ^a	r	δ^a
MP2	6-31G(d,p)	-46.42	42.13	17.84	65.22	32.61	8.3	1.6088	0.0392
	6-311++G(2df,2pd)	-56.99	30.59	6.44	68.76	34.38	10.2	1.5614	-0.0082
CCSD(T)	6-31G(d,p)	-48.13	39.45	15.30	47.24	23.62	-0.5	1.6287	0.0591
	6-311++G(2df,2pd)	-56.95	30.63	6.48	52.17	26.08	1.9	1.5885	0.0189
	aug-cc-pV6Z	-63.54	24.04	-0.11	49.82	24.91	0.8	1.5694	-0.0002
CBS-QB3		-63.47	24.11	-0.04	52.52	26.26	2.1	1.6102	0.0406
G4		-62.70	24.88	0.73	50.60	25.30	1.2	1.5925	0.0229
W1BD		-64.03	23.55	-0.60	49.61	24.80	0.7	1.5810	0.0114
PW91	6-31G(d,p)	-73.61	13.97	-10.18	49.76	24.88	0.7	1.5850	0.0154
	6-311++G(2df,2pd)	-79.68	7.90	-16.25	47.43	23.72	-0.4	1.5848	0.0152
	aug-cc-pV6Z	-81.37	6.21	-17.94	45.54	22.77	-1.4	1.5778	0.0082
TPSS	6-31G(d,p)	-64.48	23.10	-1.05	47.54	23.77	-0.4	1.5780	0.0084
	6-311++G(2df,2pd)	-70.30	17.28	-6.87	45.69	22.84	-1.3	1.5778	0.0082
	aug-cc-pV6Z	-71.71	15.87	-8.28	43.87	21.94	-2.2	1.5848	0.0152
B3LYP	6-31G(d,p)	-58.76	28.82	4.67	49.53	24.76	0.6	1.6195	0.0499
	6-311++G(2df,2pd)	-64.48	23.10	-1.05	47.87	23.94	-0.2	1.5844	0.0148
	aug-cc-pV6Z	-66.26	21.32	-2.83	45.98	22.99	-1.2	1.5736	0.0040
PBE0	6-31G(d,p)	-84.29	3.29	-20.86	51.77	25.88	1.7	1.5999	0.0303
	6-311++G(2df,2pd)	-65.58	22.00	-2.15	50.57	25.29	1.1	1.5665	-0.0031
	aug-cc-pV6Z	-67.38	20.20	-3.95	48.60	24.30	0.2	1.5563	-0.0133
M06	6-31G(d,p)	-58.66	28.92	4.77	51.26	25.63	1.5	1.5970	0.0274
	6-311++G(2df,2pd)	-64.26	23.32	-0.83	50.34	25.17	1.0	1.5661	-0.0035
	aug-cc-pV6Z	-65.54	22.04	-2.11	50.05	25.02	0.9	1.5563	-0.0133
M06-2X	6-31G(d,p)	-56.56	31.02	6.87	54.49	27.25	3.1	1.5967	0.0271
	6-311++G(2df,2pd)	-62.91	24.67	0.52	53.35	26.67	2.5	1.5633	-0.0063
	aug-cc-pV6Z	-64.38	23.20	-0.95	51.35	25.67	1.5	1.5545	-0.0151
BMK	6-31G(d,p)	-57.76	29.82	5.67	54.24	27.12	3.0	1.6199	0.0503
	6-311++G(2df,2pd)	-63.79	23.79	-0.36	53.25	26.62	2.5	1.5842	0.0146
	aug-cc-pV6Z	-65.36	22.22	-1.93	51.37	25.68	1.5	1.5693	-0.0003
B2PLYP	6-31G(d,p)	-54.20	33.38	9.23	52.43	26.21	2.1	1.6093	0.0397
	6-311++G(2df,2pd)	-61.61	25.97	1.82	52.52	26.26	2.1	1.5758	0.0062
	aug-cc-pV6Z							1.5631	-0.0065
		-63.43	24.29[b]		48.30	24.29[b]		1.5695[c]	

[a] Difference between the calculated and the experimental value.

[b] from reference [32]

[c] from reference [31]

To shed some more light on the behavior of the molecular orbital and DFT calculations we performed an extended study in which the series of basis sets cc-pVnZ and aug-cc-pVnZ, with n from 2 to 6, were used to compute the optimum geometry of the ClO, Cl_2, and O_2 molecules, their enthalpies and those of the O and Cl atoms. The results are best displayed in graphic form, showing the difference between the calculated and computed values. They are displayed in Figs 1 to 3.

Fig. 1 shows the signed error for the calculated bond lengths. The CCSD(T) values show a very nice convergence toward the experimental value. A fairly large basis set, namely aug-cc-pV5Z, is needed to decrease the error to about 2 x 10^{-3} Å.

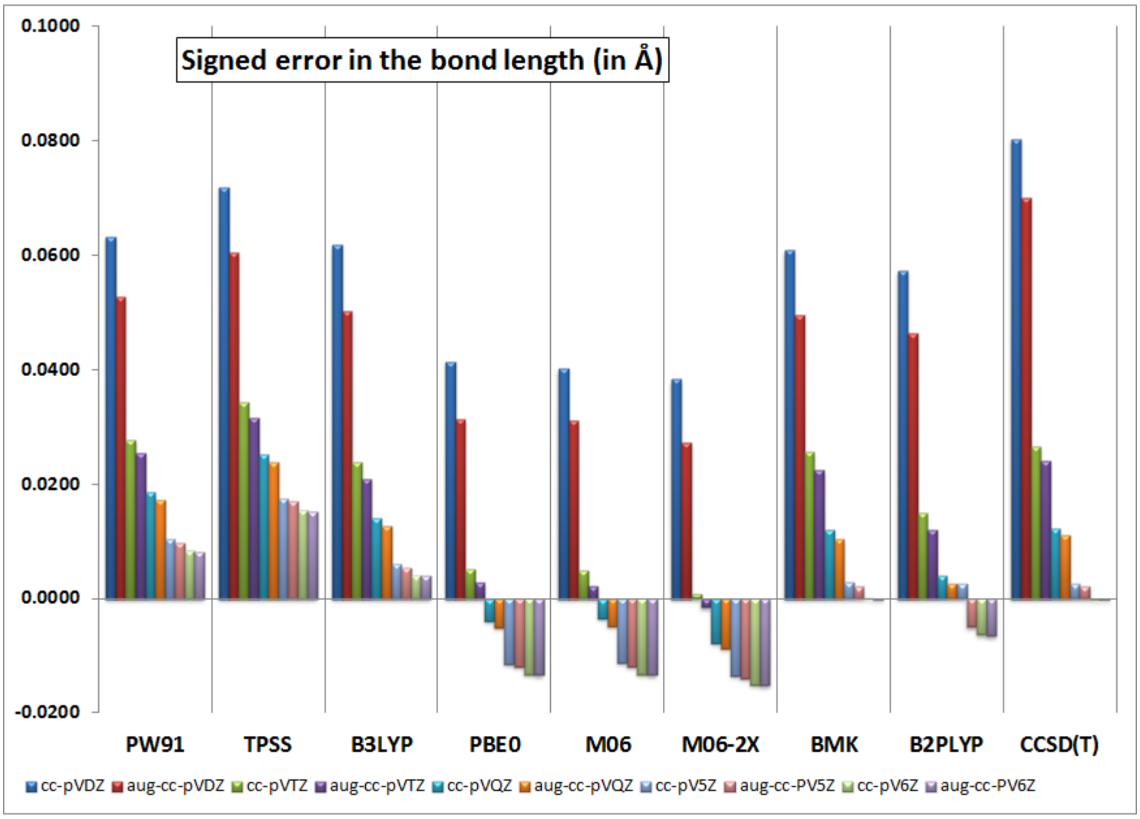


Figure 1. Difference between the optimum bond length calculated with each theoretical model and the experimental value (in Å)

The PW91, TPSS, B3lYP and BMK methods do also converge to a limit value with the increase of the basis set. Only the latter however, is able to produce errors similar to the CCSD(T) in the limit of the large basis set.

Contrary to the previous methods, the PBE0, M06, M06-2X and B2PLYP methods do not converge toward the experimental value, but to a shorter bond length. In these cases, a combination of this potential with the aug-cc-pVTZ basis set is the best choice to get fairly accurate results at minimum cost. Purely from the point of view of obtaining the best bond length, the M06-2X/cc-pVTZ or M06/aug-cc-pVTZ models are the best options. If the CCSD(T) method was used for the optimizations with these same basis sets, the error would be ten times larger. Thus, it is clear that error compensation makes sufficiently complex

DFT methods to have the advantage over the more theoretically sound CCSD(T) procedure with respect to geometry optimizations. Let us see what happens in terms of energies.

When the enthalpy of formation of ClO is obtained from reaction (1) the results are those depicted in Figure 2. CCSD(T) converges monotonically toward the experimental value, while all the DFT methods do converge toward a smaller enthalpy of formation. The results obtained with the PW91 and TPSS rule out these methods with any basis set. In fact, the results worsen systematically with the increase of the basis set. The best results in this case are obtained with the M06/cc-pVQZ model. Similar results are obtained with the B3LYP/cc-pVTZ, PBE0/cc-pVTZ and BMK/cc-pVQZ models, although in these cases it is clear that the convergence of the models with the increase of the basis set is toward a much smaller enthalpy of formation. Both the M06-2X and the B2-PLYP method afford a good value with a relatively small basis set and converge to a value around 1 kcal/mol lower than the experimental one. B2PLYP calculations are, of course, much more demanding than M06-2X (although not so much as the CCSD(T) ones). Although larger, the cc-pVQZ basis set is comparable to the 6-311++G(2df,2pd) Pople set. The results obtained with the M06 methods are then comparable also (24.83 and 24.29 kcal/mol) and close to the experimental one.

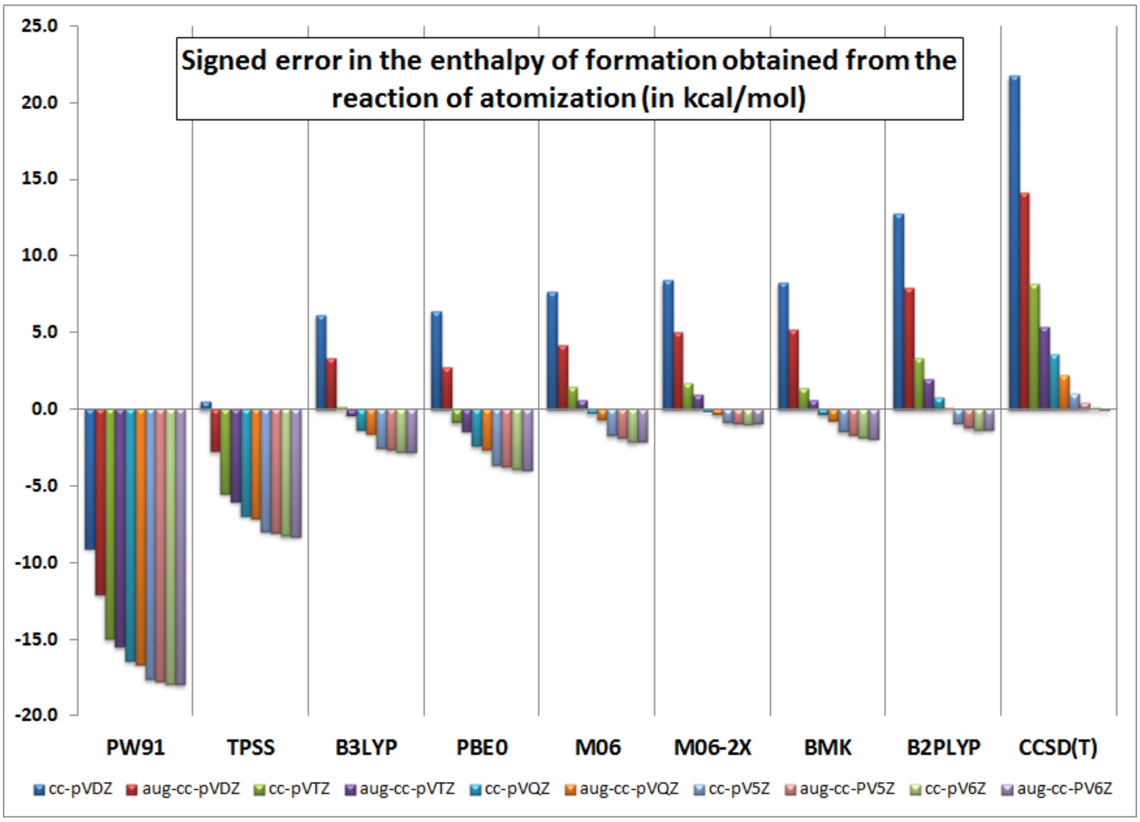


Figure 2. Difference between the enthalpy of formation of ClO at 298.15 K obtained from the reaction of atomization (1) with the experimental value (in kcal/mol)

If the enthalpy of formation is obtained from the enthalpy of reaction of the diatomics, the results are those depicted in Figure 3. The largest error of each model is now much lower than when the enthalpy of formation was obtained from the atomization energy, a fact probably due to the less than perfect description of the atoms provided by the smaller basis sets. When the basis sets are large enough, the results are definitely better. For instance, the largest difference between theoretical calculations and the experimental value is -2.4 kcal/mol for the TPSS/aug-cc-pV6Z model, which is not too much worse than the 0.8 kcal/mol obtained at the much more demanding CCSD(T)/aug-cc-p6Z level and much better than the -7.4 kcal/mol error obtained when the enthalpy of formation was obtained at the same level from the TAE, reaction (1).

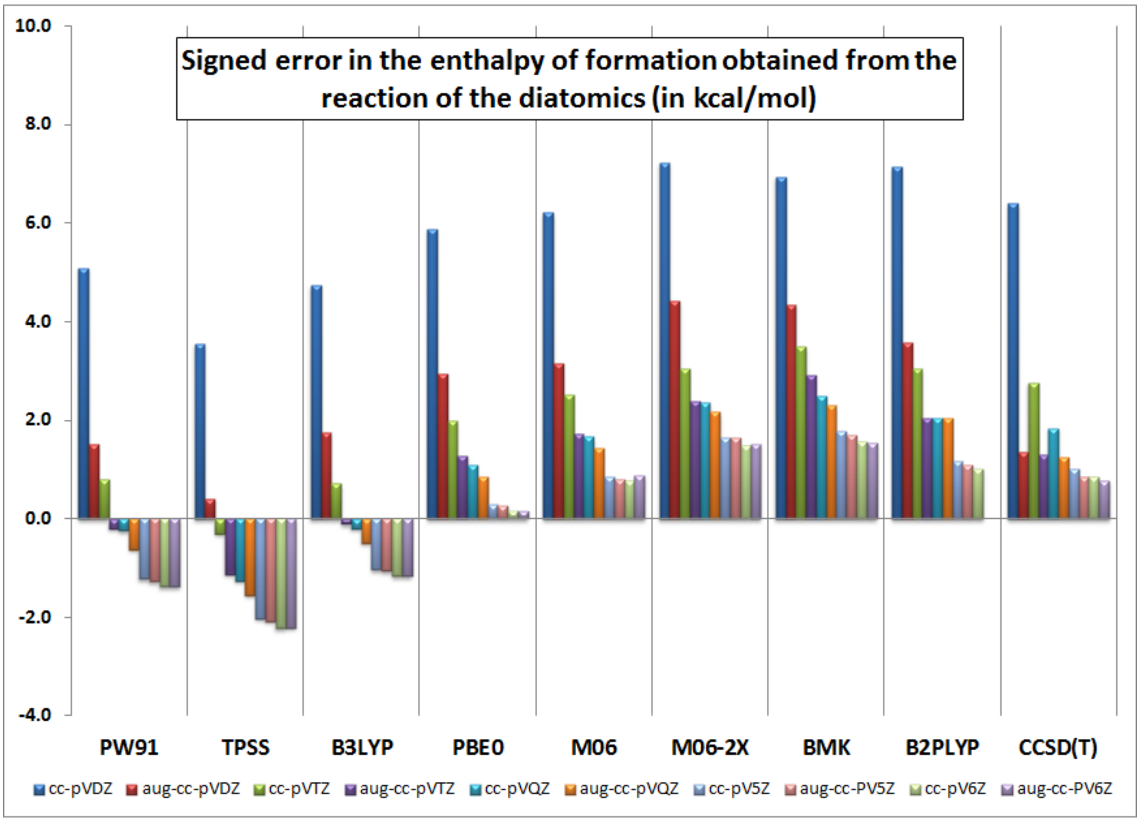


Figure 3. Difference between the enthalpy of formation of ClO at 298.15 K obtained from the reaction of diatomic chlorine and oxygen, reaction (2), and the experimental value (in kcal/mol)

In the case of reaction (2) there is a residual error in the calculation of the enthalpy of formation, due to the presence of the doublet radicals in the lhs of the equation while a triplet is present in the rhs. PW91, TPSS, B3LYP and PBE0 exhibit some error compensation and then models like PW91/aug-cc-PVTZ, TPSS/cc-pVTZ, B3LYP/cc-pVTZ and PBE0/cc-pV5Z or larger give results very similar to the experimental ones. For the rest of the methods, only M06 and B2PLYP with basis sets cc-pV5Z (or larger) are able to give results with similar accuracy than the CCSD(T) calculations at the same basis set level. However, M06 using the cc-pVQZ basis set is able to give also an error below 1.5 kcal/mol which is acceptable in terms of cost/benefit analysis.

Taking the three sets of results, the bond length and the enthalpy of formation obtained from both reactions (1) and (2), we may conclude that the M06/cc-pVQZ calculations give a reasonable description of the ClO bond. The respective errors are -0.003 Å, 0.5 kcal/mol and 1.5 kcal/mol. Using the same basis set, the errors of the CCSD(T) calculations are 0.012 Å, 4.4 kcal/mol and 1.7 kcal/mol, with a much larger computing effort.

HClO/HOCl isomers.

The reaction of ClO with a hydrogen atom is the simplest possible route for the formation of a closed shell species. Two isomers can be formed depending on the oxidation state of chlorine, H-O-Cl and H-Cl=O. These isomers have been extensively studied, both theoretically and, at least for the first isomer, also experimentally.

Ashby in 1967 studied experimentally the IR spectrum of HOCl at high resolution [38]. They determined the bent geometry of this molecule as r(OH)=0.974 ± 0.02 Å, r(OCl) = 1.689 ± 0.006 Å and ∠HOCl = 104.78 degrees. Mirri et al [39] a little later refined this structure studying the rotational spectra of several isotopic variants of HClO. The geometric parameters found were r(OH)=0.975 ± 0.003 Å, r(OCl) = 1.6895 ± 0.0035 Å and ∠HOCl = 102.48 ± 0.45 degrees. We chose to use the parameters selected by the authors themselves, because a relatively large error in the r(OH) distance was noticed depending on which inertia defects were chosen for the derivation. A value as small as 0.960 Å was reported for the r(OH) bond length. More recently, a detailed analysis of the vibration-rotation spectra of deuterated HOCl was performed by Deely [40]. The r_e structure determined yield the values r(OH)=0.9643 ± 0.0005 Å, r(OCl) = 1.6891 ± 0.0002 Å and ∠HOCl = 102.96 ± 0.08 degrees. We will use these values to compare against the theoretically calculated ones.

Experimental determination of the enthalpy of formation of HOCl has been performed several times. The values determined at 298K, -17.8 kcal/mol [41] [42], -18.0 kcal/mol [43], -17.9 kcal/mol [44] and -18.0 ± 0.9 kcal/mol [45], are quite consistent. These determinations were obtained based on the equilibrium constant of the reaction

$$H_2O(X^1A_1) + Cl_2O(X^1A_1) \rightarrow 2HOCl(X^1A') \qquad (3)$$

The most recent determination at 0K is that of Joens using thermochemical cycles [46], who obtained a value of 17.68 ± 0.03 kcal/mol. The net reaction used by Joens was

$$H_2(X^1\Sigma_g^+) + Cl_2(X^1\Sigma_g) + O_2(X^3\Sigma_g^-) \rightarrow 2HOCl(X^1A') \qquad (4)$$

Several theoretical studies have been performed on this molecule. Hirsch et al [47] performed MRD CI calculations with small basis sets on this species in 1977. They assumed a fixed geometry using the microwave determined values of Mirri et al [39] and calculated the enthalpy of formation of HClO among other properties. Depending on the reaction scheme used to calculate the enthalpy of formation, they obtained values ranging from -24.1 to -14.8 kcal/mol. Francisco and Sander [48] performed QCISD(T) calculations using the Pople 6-311++G(3df,3pd) basis set on top of a geometry optimized at a simpler level. This geometry reproduced reasonably well the H-O bond (0.963 Å) but not the Cl-O bond which was about 0.05 Å longer than the experimental one. The enthalpy of formation was obtained using the isodesmic reaction

$$\mathrm{HOCl}(\mathrm{X}^1\mathrm{A}') + \mathrm{HO}(\mathrm{X}^2\Pi) \rightarrow \mathrm{H_2O}(\mathrm{X}^1\mathrm{A}_1) + \mathrm{ClO}(\mathrm{X}^2\Pi) \qquad (5)$$

The best result obtained was -19.9 ± 2 kcal/mol, in reasonable agreement with the experimental determinations. Lee in 1994 [49] performed CCSD(T) geometry optimizations with a TZ2P basis set and CCSD(T) with ANO basis sets on top of those optimized geometries to obtain different properties of HClO and other related molecules. Again the r(OH) distance was well represented while the r(OCl) bond was too large. Denis in 2006 [50] estimated the enthalpy of formation of HOCl from the atomization reaction employing CCSD(T) with correlation consistent basis sets and corrections for core-valence, relativistic, and anharmonic effects. The correlation consistent cc-pVQZ basis set was used for geometry optimizations and extrapolation to the complete basis set was used for the energies. The enthalpy of formation of HOCl was calculated as -18.1 ± 0.3 kcal/mol which may be considered to be the most accurate value calculated up to date. This value is in very good agreement with the value calculated later by Karton et al [35], -18.20 ± 0.14 kcal/mol, using essentially the same methodology. Finally, another work worth citing was published by Meyer and Kass in 2010 [51] who performed a comparison between the results obtained with several density functional methods and those obtained at the CCSD(T) level using correlation consistent basis sets up to cc-pV(Q+d)Z level. The best result obtained at the W4 level was -18.2 ± 0.1 kcal/mol (same, of course, as Karston et al did at the same level), to be compared with M06-2X and M06 results of -17.7 and -16.5 kcal/mol using the same basis set.

There is not so detailed information about the less stable HClO isomer. No experimental values are available neither for the geometry of this species nor for the enthalpy of formation. Theoretical studies do exist, starting with the aforementioned study of Lee [49], another one performed by Hernandez et al in 1999 [52] and the most recent one by Peterson and coworkers [53] at the MRCI+Q/CBS level. The ClO bond is calculated as 0.13 Å shorter in HClO than in HOCl and both isomers are separated by a 73.5 kcal/mol barrier. At this level of calculation, the HClO isomer is 53.7 kcal/mol less stable than HOCl. A similar result was reported by Jalbout [54] who performed B3LYP and CCSD(T) calculations using Pople's 6-311++G(3df,3pd) basis set. He found activation barriers of 76.1 kcal/mol and 70.1 kcal/mol at each level, while the HClO isomer was found to lie 54.5 kcal/mol and 52.5 kcal/mol respectively above the HOCl isomer.

The geometry optimization at the CCSD(T)/aug-cc-pV6Z performed in this paper for HOCl is the more extensive we are aware of. Even if the molecule is pretty small, the need to calculate integrals with up to *i* Gaussian functions for oxygen and chlorine as well as *h* functions for hydrogen, represents a sizeable challenge. Similar to the case of ClO, for which the calculated ClO distance was only 0.0001 Å smaller than the experimental one, in this case the difference is also very small. The geometric parameters obtained at the CCSD(T)/aug-cc-pV6Z level, r(OH)=0.9644 Å, r(OCl)=1.6899 Å and ∠HOCl = 102.95 deg are in extraordinary good agreement with Deely's experimental values *r*(OH)=0.9643 ± 0.0005 Å, *r*(OCl) = 1.6891 ± 0.0002 Å and ∠HOCl = 102.96 ± 0.08 deg [40]. A graphical comparison of the errors in the estimation of the r(OCl) bond length with different DFT methods and the CCSD(T) method using the Dunning basis sets is depicted in Fig. 4

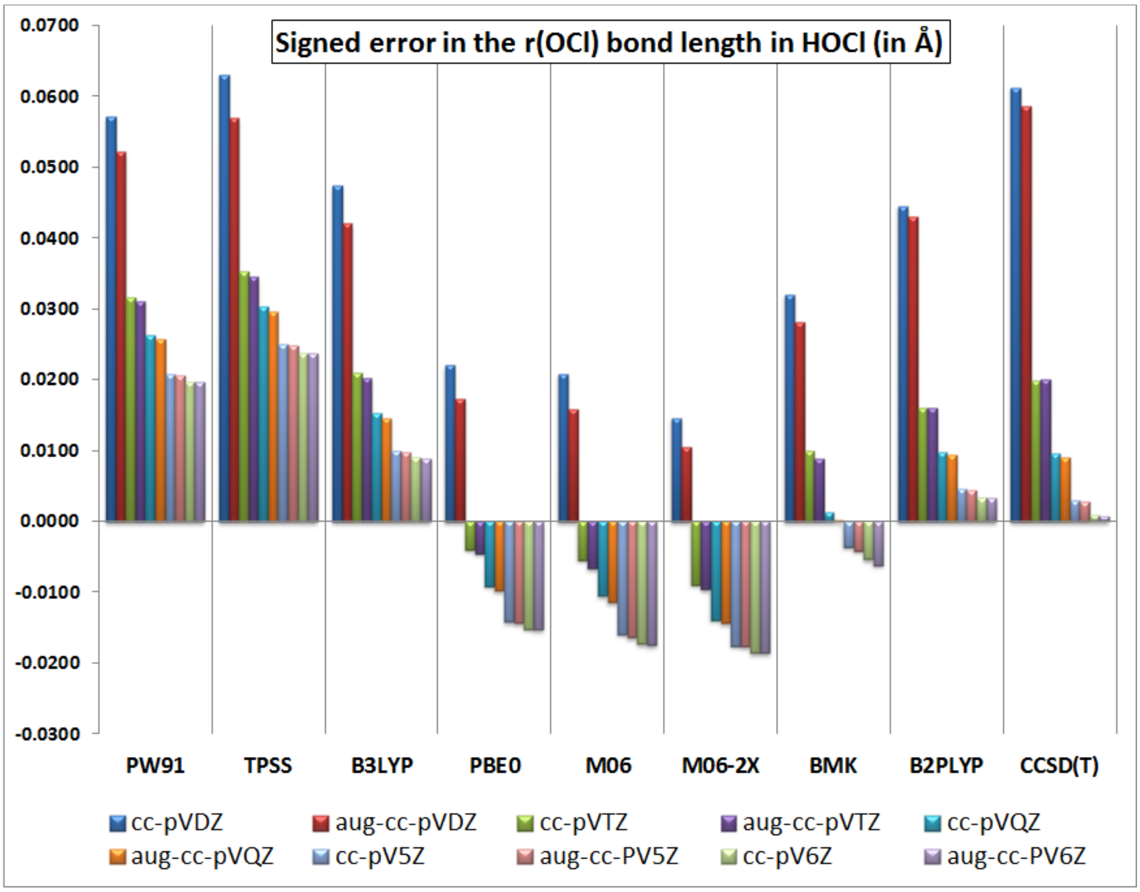


Figure 4. Signed error of the calculated r(OCl) bond distance with respect to the experimental one determined bye Deely, see text (in Å)

The optimum geometry calculated using the cc-pVQZ basis set at the CCSD(T) level, as done previously, affords an absolute error which is similar to that obtained at the B2PLYP or PBE0 levels, and larger than that obtained using the BMK method. From the aspect of the graphs it is clear that this is due to error compensation. As in the case of ClO, CCSD(T) calculation of geometries using a moderately large basis set like cc-pVQZ are not better than those obtained with the much cheaper DFT calculations. However, in this case, neither M06 or M06-2X are able to give as good results as those obtained for the ClO radical.

As we said before, there is no experimental value for the structure of HClO. Our best result at the CCSD(T)/aug-cc-pV6Z level is r(HCl)=1.3094 Å, r(ClO)=1.5568 Å and ∠HOCl=107.75 degree. The parameters calculated by Peterson and coworkers at the MRCI+O level with an aug-cc-pVQZ basis set are r(HCl)=1.3066 Å, r(ClO)=1.5625 Å and ∠HOCl=107.81 degree. The most interesting result to be observed from these data concerns the bond order of the ClO bond in the ClO radical.

In Table 2 we show the optimum ClO bond lengths obtained at different levels of theory for the three species HClO, ClO and HOCl. The ClO bond in HOCl is a single bond, while in HClO we have a double bond. What is then the bond order in ClO? Two models were chosen. One was the simple linear correlation between bond order and bond length, while the second was Pauling´s exponential correlation between the bond order and the difference of the observed bond length and that of a single bond. In the first case, the bond order derived from the CCSD(T)/aug-cc-pV6Z model (same results are obtained from DFT methods) is 1.89, while in the second case is 1.87. These congruent results imply that the bond order in ClO is much nearer to a double bond than to a single bond and the structure more similar to $^\bullet$Cl=O than to Cl-O$^\bullet$. It means that the solitary electron density distribution is located mainly on the chlorine atom and not the oxygen atom.

Several reactions can be used to calculate the enthalpy of formation of HClO and HOCl. Obviously the reaction of atomization, as well as reaction (4) can be used to obtain the enthalpy of formation of both isomers. Reaction (3) is isodesmic between closed shell molecules and can be used to calculate the enthalpy of formation of HOCl. Reaction (5) in turn is also isodesmic and isogyric (a doublet radical species is present in both the lhs and rhs of the equation). Combining reactions (3) and (5) one can obtain another reaction, which can be written as

$$\mathrm{HOCl}(X^1A') + \mathrm{ClO}(X^2\Pi) \rightarrow \mathrm{HO}(X^2\Pi) + \mathrm{Cl_2O}(X^1A_1) \qquad (6)$$

Comparison of the enthalpies of formation obtained from reactions (5) and (6) with those obtained from reaction (3) will provide us with some indications about errors involved in the calculations.

For the case of HClO we can also formulate a pair of other reactions which can be used to obtain the enthalpy of formation. These reactions are

$$\mathrm{HClO}(X^1A') + \mathrm{Cl}(^2P) \rightarrow \mathrm{HCl}(X^1\Sigma^+) + \mathrm{ClO}(X^2\Pi) \qquad (7)$$

$$\mathrm{HClO}(X^1A') + \mathrm{ClO}(X^2\Pi) \rightarrow \mathrm{HCl}(X^1\Sigma^+) + \mathrm{OClO}(X^2B_1) \qquad (8)$$

Table 2. Optimum ClO bond length (in A) calculated at different theoretical levels for the three species HClO, ClO and HOCl

Species	Method	**6-31G(d)**	**6-311++G(2df.2pd)**	**aug-cc-pV6Z**
HClO	MP2	1.5961	1.5492	
	CCSD(T)	1.6493	1.5806	1.5568
	PW91PW91	1.6095	1.5720	1.5566
	TPSSTPSS	1.6200	1.5785	1.5626
	B3LYP	1.6262	1.5775	1.5594
	PBE0	1.5955	1.5539	1.5381
	M06	1.5944	1.5496	1.5310
	M06-2X	1.6117	1.5643	1.5501
	BMK	1.6350	1.5869	1.5646
	B2PLYP	1.6216	1.5715	1.5540
ClO	MP2	1.6088	1.5614	
	CCSD(T)	1.6287	1.5885	1.5694
	PW91PW91			1.5778
	TPSSTPSS			1.5848
	B3LYP	1.6195	1.5844	1.5736
	PBE0	1.5999	1.5665	1.5563
	M06	1.5970	1.5661	1.5563
	M06-2X	1.5967	1.5633	1.5545
	BMK	1.6199	1.5842	1.5693
	B2PLYP	1.6093	1.5758	1.5631
HOCl	MP2	1.7183	1.6946	
	CCSD(T)	1.7355	1.7072	1.6899
	PW91PW91	1.7384	1.7158	1.7088
	TPSSTPSS	1.7419	1.7197	1.7128
	B3LYP	1.7272	1.7053	1.6980
	PBE0	1.7010	1.6807	1.6739
	M06	1.6987	1.6785	1.6717
	M06-2X	1.6940	1.6765	1.6706
	BMK	1.7125	1.6917	1.6830
	B2PLYP	1.7235	1.7017	1.6924

Both for reactions (6) and (8) we need to calculate two of the XOCl isomers (X=O and Cl) which we will describe in detail later. For the moment we will use their enthalpies to calculate the enthalpies of reaction we need only. Suffice it to say that, as in the case of the other molecules, full geometry optimization at each level of calculation (method + basis set) was performed for H_2, HO, H_2O, HCl, OClO and ClOCl, the additional species we need to obtain the enthalpies of reactions (3) to (8).

The full table with the enthalpies of reaction and derived enthalpies of formation for HOCl and HClO are given in the Additional Material. In the following we will analyze those numbers in two ways. On the one side, we are interested in knowing how the enthalpies converge with the basis set, given a certain method, for all reactions. On the other, we are interested in knowing how do the results converge for all methods and basis sets in the case of each of the reactions.

A general overview of the results obtained for the enthalpy of formation of HOCl is shown in Figures 5 and 6. In Fig. 5 we show the convergence with the increase of the basis set of the enthalpy of formation of HOCl extracted from each one of the reactions at the CCSD(T) level. Full lines show the results obtained from the reactions in which mostly closed shell species participate (the only exception is the triplet oxygen molecule). The results obtained from reaction (3) are slightly too negative, the best value being -18.80 kcal/mol which is within the error limits determined experimentally by Ennis and Birks, -18.0 ± 0.9 kcal/mol [45], using the equilibrium constant of the same reaction. As we said before, this isodesmic reaction can be considered as the composing of reactions (5) and (6) which results are represented in Fig. 5 using dotted lines. It is clear that the error is larger in both cases, but to opposite directions, so that they compensate in the calculation derived from reaction (3).

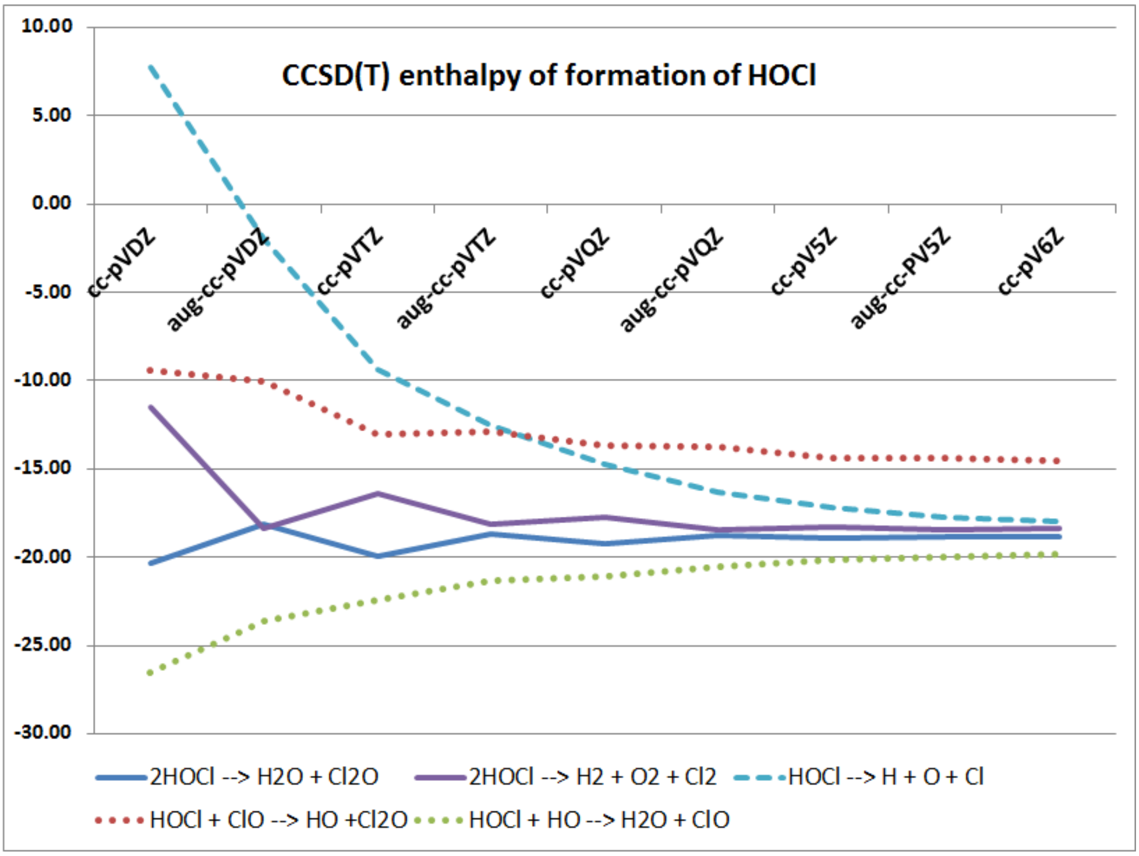


Figure 5. Enthalpies of formation of HOCl (in kcal/mol) obtained at the CCSD(T) level using different basis sets and reactions (3) to (6)

The limit result obtained from reaction (4) is -18.45 kcal/mol. The errors with each basis set are similar to those of the determination from reaction (3). The less negative result for the enthalpy of formation is in agreement with the experimental determination of Joens [46] (the difference in the enthalpy of formation at 0 and 298K is around 0.05 kcal/mol).

Finally, the dashed line represents the enthalpy of formation obtained from the TAE (without any of the corrections used by Denis [50], Karton et al [35] or Meyer and Kass [51] using the W4 method). Our best result is -18.15 kcal/mol, within the error limits of the values reported by the former authors, -18.1 ± 0.3 kcal/mol [50], -18.20 ± 0.14 kcal/mol [35], and -18.2 ± 0.1 kcal/mol [51]. It may be concluded then that, as was discussed in the case of ClO, no significant improvement is obtained in the determination of the enthalpy of reaction of HOCl using methods beyond CCSD(T) with an extended basis set both for geometries and energies.

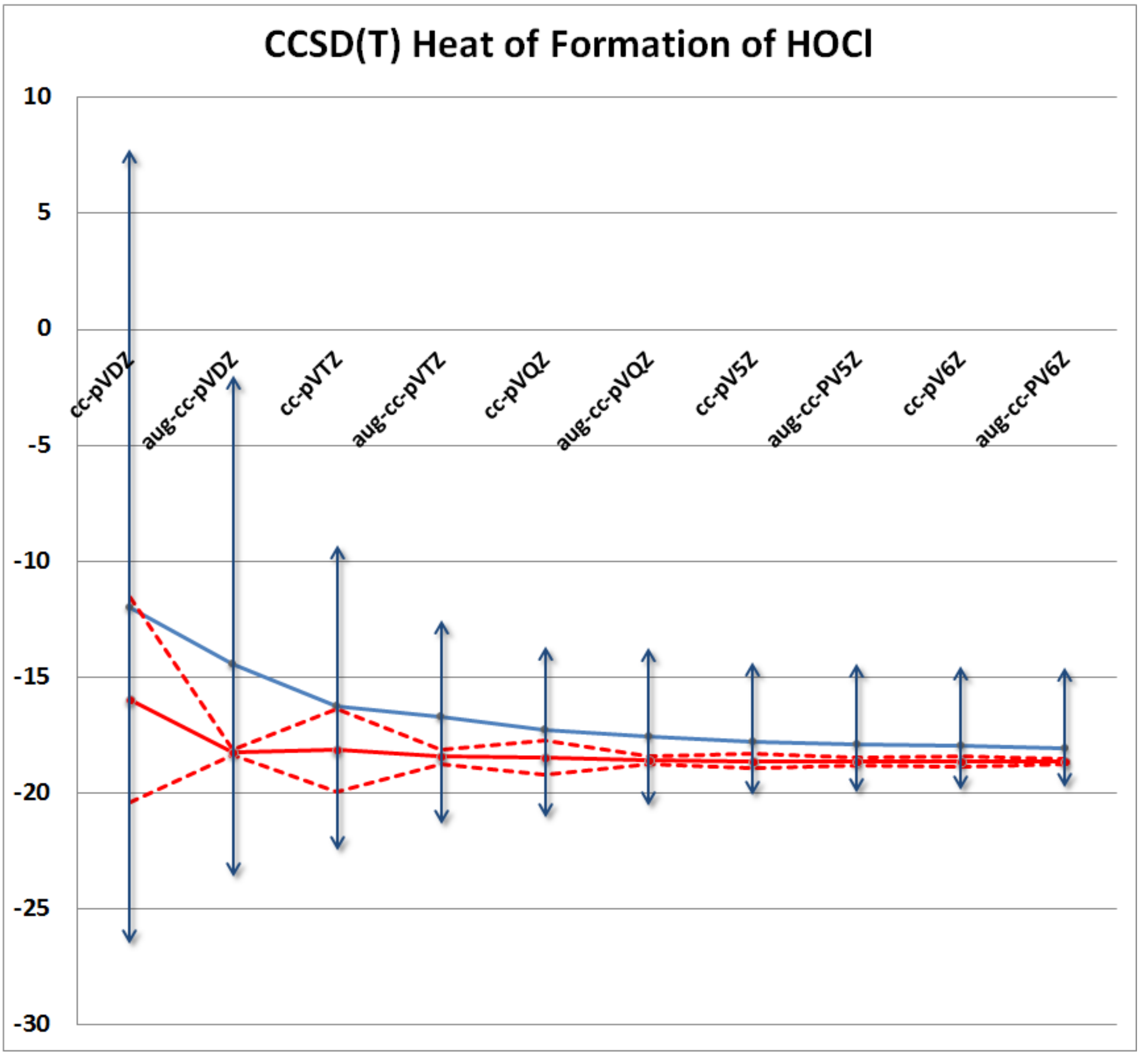


Figure 6. Average values and maxima and minima of the enthalpy of formation of HOCl obtained from the five reactions considered (in red) or only from reactions (3) and (4) (in blue)

Since all the reactions employed for obtaining the enthalpy of formation seem to exhibit some degree of error and error cancellation, one can aim to obtain the enthalpy of formation as an average of the values derived from the different reactions. In Figure 6 there is a graphical representation of the convergence of the average, as well as maximum and minimum values, for the CCSD(T) calculations. On one side, the values obtained from the five reactions considered were averaged. This is shown in blue. On the other side, only the values obtained from reactions (3) and (4) (red dotted lines) were averaged (red continuous line). The conclusion is that the average obtained from all the reactions, -18.05 kcal/mol, is smaller and more in agreement with the experimental results than that obtained from only reactions (3) and (4), -18.64 kcal/mol, but in all cases in reasonable agreement with previous accurate theoretical determinations.

Fig. 7 shows an overview of the results obtained for different methods, basis sets and reactions. The upper panels show the behavior of different methods with respect to the reactions. It is immediately obvious that the results obtained from the isodesmic reaction (3) are mostly independent of the basis set and the method, giving the more consistent results. If the TAE would be used instead, the PW91 method gives very bad values, but no one would use it anyway. Taking the diatomic molecules as reference, instead of the atoms, reaction (4), give reasonable results (except for TPSS which, again, is a bad choice) but with more dispersion in the limit and smaller than those obtained from reaction (3). Finally, the results obtained from reaction 5 and reaction 6 (not shown) do exhibit larger errors and dispersion of the limit results.

The lower panels show the convergence with the basis sets of the results obtained with some of the methods for the five reactions. The general behavior of the depicted DFT results is similar to that of the CCSD(T) calculations. However, the dispersion of the values obtained from each reaction using the smaller basis sets is larger for CCSD(T) than for the DFT methods. At the large basis set limit however, the DFT methods, especially M06, converge toward a very similar value than CCSD(T) especially if the average of reactions (3), (4) and the TAE are considered. Using a not so large cc-pV5Z basis set, the average results for M06, M06-2X, B2PLYP and CCSD(T) are -18.0, -18.7, -17.3 and -18.3 kcal/mol.

A final analysis can be performed comparing the results obtained using the same methods and basis sets for HOCl and HOH. In Table 3 are shown the results obtained for the enthalpy of formation of HOH and HOCl using the CCSD(T) method with the series of Dunning basis sets, obtained from the enthalpy of reaction of the atomization reaction and the formation from the diatomics in each case.

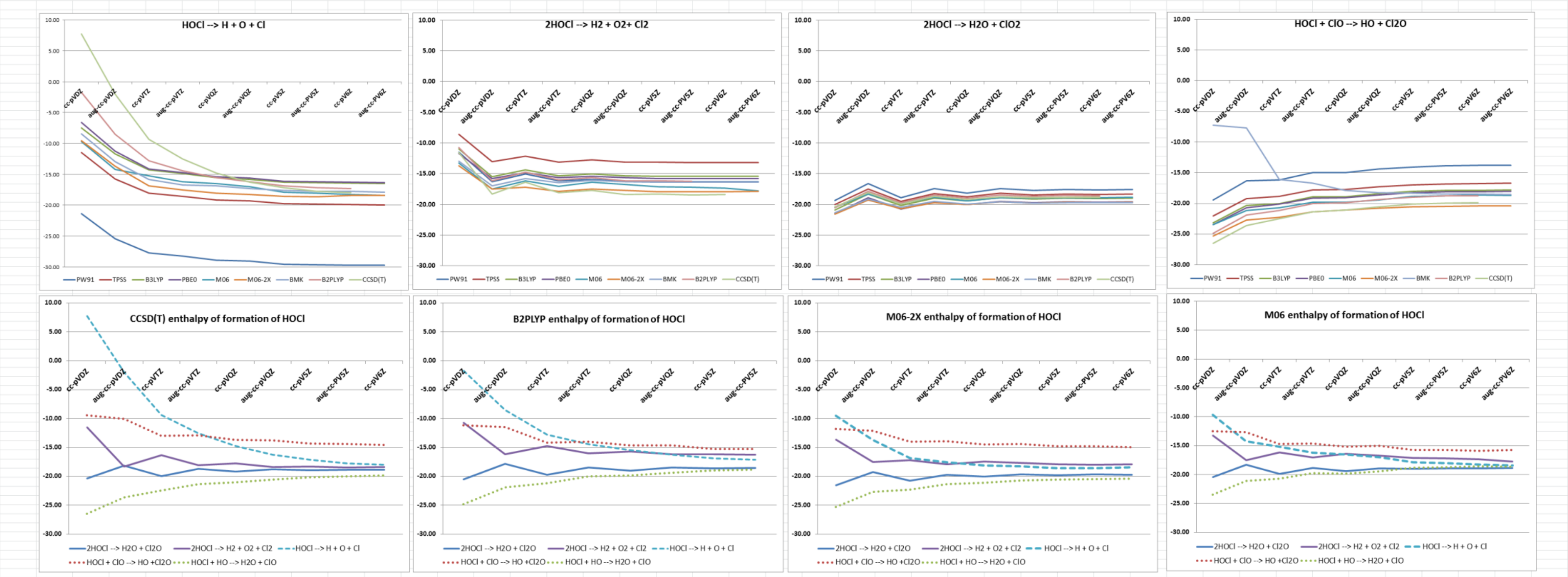


Figure 7. Comparison of the enthalpies of formation derived from different reactions with several methods and basis sets (upper panels) and for each method with several basis sets from several reactions (lower panels). All enthalpies of formation are in kcal/mol. See the text for further discussion.

Table 3. Enthalpies of reaction and derived standard enthalpies of formation (in kcal/mol) for water and hypochlorous acid using different models

Basis set	H2O				HOCl			
	$HOH \rightarrow 2H + O$		$HOH \rightarrow H_2 + 1/2O_2$		$HOCl \rightarrow H + Cl + O$		$2HOCl \rightarrow H_2 + Cl_2 + O_2$	
	ΔH^o_r	ΔH^o_f	ΔH^o_r	ΔH^o_f	ΔH^o_r	ΔH^o_f	ΔH^o_r	ΔH^o_f
cc-pVDZ	197.41	6.05	47.85	-8.15	132.90	7.75	23.09	-11.55
aug-cc-pVDZ	208.10	-4.64	56.56	-16.86	142.63	-1.98	36.66	-18.33
cc-pVTZ	213.61	-10.15	54.52	-14.82	150.00	-9.35	32.72	-16.36
aug-cc-pVTZ	216.91	-13.45	57.01	-17.31	153.20	-12.55	36.20	-18.10
cc-pVQZ	218.44	-14.98	56.84	-17.14	155.41	-14.76	35.46	-17.73
aug-cc-pVQZ	219.79	-16.33	57.71	-18.01	156.93	-16.28	36.83	-18.41
cc-pV5Z	220.09	-16.63	57.65	-17.95	157.81	-17.16	36.59	-18.30
aug-cc-PV5Z	220.49	-17.03	57.80	-18.11	158.43	-17.78	36.94	-18.47
cc-pV6Z	220.62	-17.16	57.78	-18.09	158.66	-18.01	36.81	-18.40
aug-cc-PV6Z	220.77	-17.31	57.81	-18.11		-18.15		-18.45

The results are depicted graphically in Fig. 8, where the values for the enthalpy of formation of water has been shifted upward by the difference of the experimental enthalpies of formation of both species, so as to compare the curves more easily.

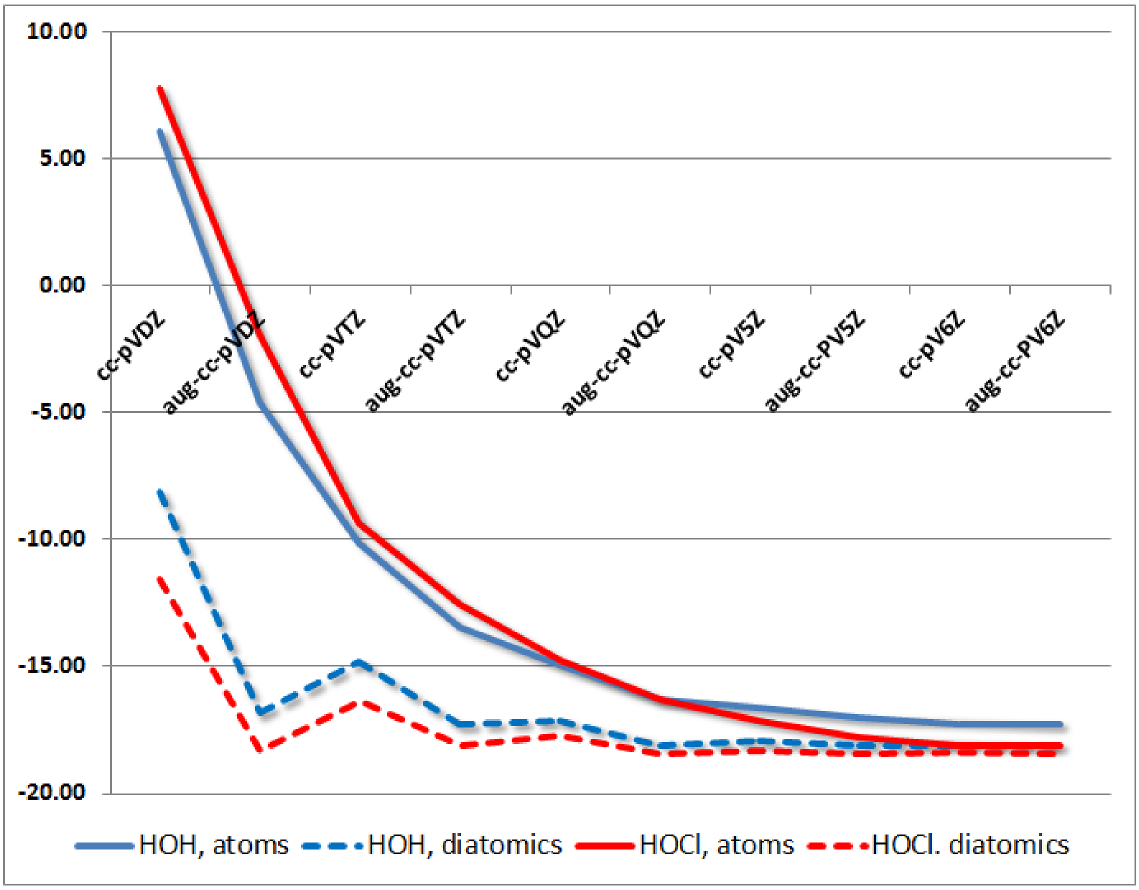


Figure 8. Convergence of the CCSD(T) standard enthalpies of formation of H2O and HOCl (in kcal/mol) obtained from the atomization reaction and the decomposition toward the diatomics. The values for water have been shifted upwards by the difference between the experimental enthalpies of formation, 39.7 kcal/mol

Several conclusions can be obtained from this comparison. On the one hand, the convergence of the values for the enthalpy of formation of HOCl with both reactions is more precise than that for H_2O. On the other hand, although the series converge to very similar values in each case, the values obtained with the participation of th diatomics is converged much faster than when the enthalpy of formation is obtained from the TAE. Using the cc-pVQZ basis set the values obtained from reaction (4) are well converged, while those obtained from the TEA are still several kcal/moll off the mark. Finally, the agreement between the values obtained from both reactions show that, at least for closed shell molecules, it is unnecessary to include post-(T) effects, since triple, quadruple and quintuple excitation contributions tend to cancel with the contributions from core correlation, relativistic and spin-orbit corrections.

In the case of HClO we don´t have experimental values with which to compare. We will derive the enthalpy of formation using the TAE, the decomposition to diatomics (similar to equation (4) with HClO instead of HOCl) and the other two isodesmic reactions (7) and (8). Additionally, we will also use reaction (3) which is not isodesmic in the case of HClO. It will provide us with a measure of the suppression of errors produced by the isodesmicity.

We show in Table 4 the enthalpies of formation obtained from each of the reactions and the energy difference between the isomers, employing different methods and the largest basis set in each case.

Table 4. Standard enthalpies of formation of HClO (in kcal/mol) obtained from the reaction of atomization and reactions (3), (4), (7) and (8) are reported in the first five columns of the table. The energy difference between HClO and HOCl (without zero-point energies) is shown in the sixth column. The last column shows the average of the enthalpies of formation calculated using reactions of atomization, (4), (7) and (8). Values obtained with reaction (3) were not included in this average. The last file shows the averages, for each reaction, of the values of the enthalpy of reaction obtained with each method, excluding the PW91 and TPSS values.

			Reaction			ΔE	
	TEA	**(4)**	**(8)**	**(7)**	**(3)**	**HClO-HOCl**	**Average**
PW91	16.3	29.7	37.4	33.7	12.0	48.1	**29.3**
TPSS	26.6	33.3	34.6	34.4	3.5	48.6	**32.2**
B3LYP	33.1	34.2	32.1	33.8	6.5	51.7	**33.3**
PBE0	32.3	32.8	34.4	33.8	32.4	50.6	**33.3**
M06	31.9	32.5	35.8	33.3	19.5	51.8	**33.4**
M06-2X	33.7	34.2	30.1	33.1	20.4	54.3	**32.8**
BMK	34.9	36.3	31.6	35.8	23.1	55.0	**34.6**
B2PLYP	32.9	33.9	37.2	32.5	21.3	54.8	**34.2**
CBS-QB3	32.3	34.0	35.8	32.5	34.7	51.6	**33.7**
G4	33.9	33.6	34.7	31.8	34.8	51.6	**33.5**
W1BD		32.7	34.7	33.1	34.4	51.6	**33.5**
CCSD(T)	33.5	33.1	34.5	33.0	40.6	53.5	**33.5**
Average	**33.2**	**33.7**	**34.1**	**33.3**	**26.8**		

The energy difference between the isomers, calculated at the CCSD(T)/cc-pV6Z level, 53.5 kcal/mol, is in complete agreement with that found by Peterson et al [53]. Using the smaller basis set employed by Jalbout [54], the result is only 1 kcal/mol lower, so that there is not a large influence of the basis set in this property. Except for the less precise PW91 and TPSS models, all the DFT and compound ab initio calculations give results in the 50-55 kcal/mol range. Thus, the barrier is not heavily dependent on the method used either.

The result obtained averaging the values for the enthalpy of formation across methods and reactions is 33.6 ± 2.8 kcal/mol (error calculated as 2σ). Because of their obvious inaccuracy, we have left out of this average both the results obtained with the PW91 and TPSS methods and the results obtained from reaction (3). The lack of isodesmicity of this reaction for HClO implies that no error cancellation is occurring and the results are thus much worse than when the same reaction was used for calculating the enthalpy of formation of the HOCl isomer, for which (3) is truly isodesmic.

The behavior of different methods of calculation of the enthalpy of formation of HClO can be seen in Fig. 9.

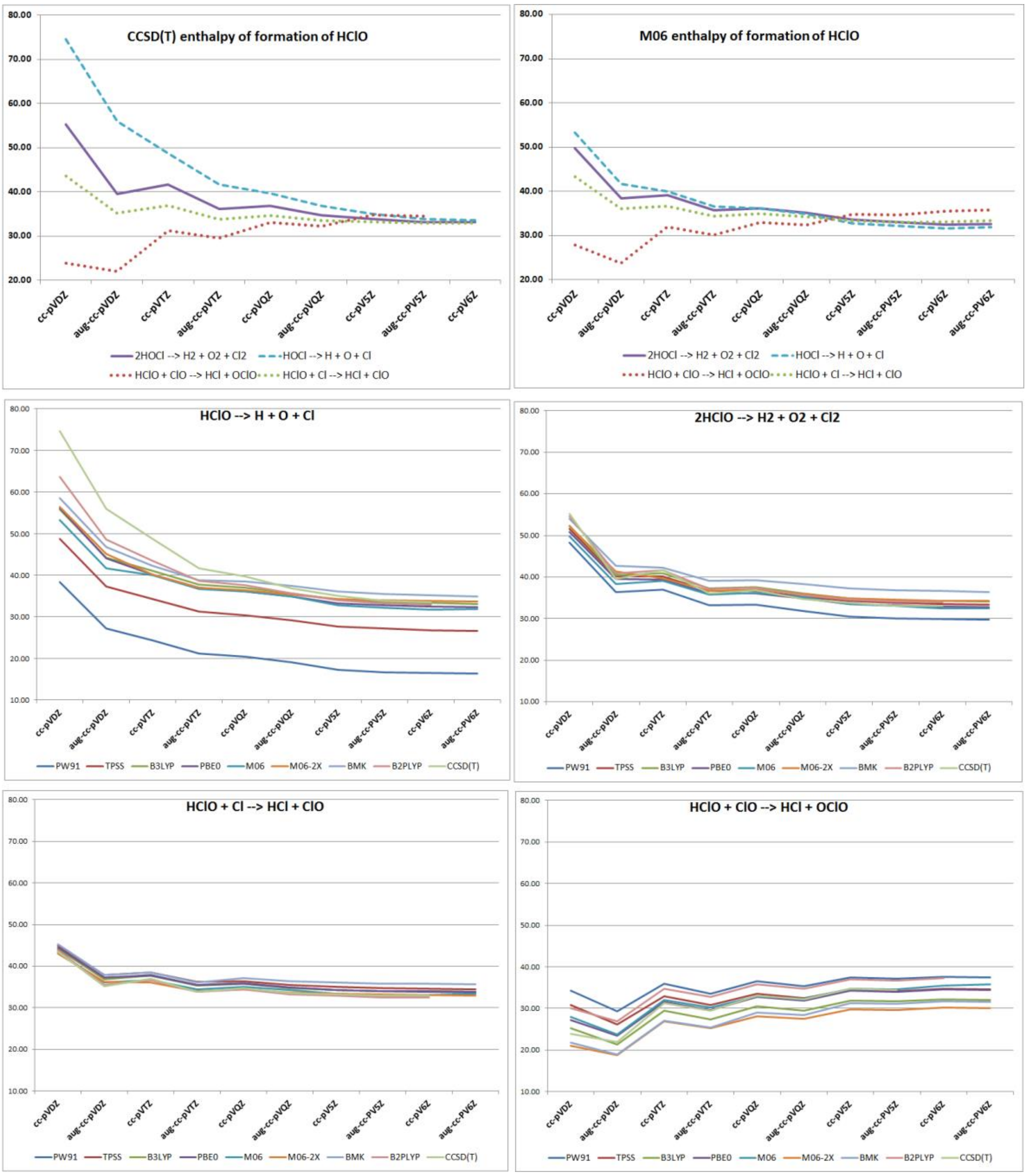


Figure 9. Convergence of the values of the enthalpy of formation of HClO (in kcal/mol) for differente reactions and models. The CCSD(T) and M06 results are shown in the upper two panels for each of the four reactions considered. The lower four panels show the convergence of all methods for each one of the four reactions.

The most important observation is the very small dispersion of the values of the enthalpiy of formation calculated with different chemical models from reaction (7). This is another indication that the unpaired electron in the ClO radical is located mainly on the chlorine atom, since the errors associated to the radical in the rhs of the reaction are clearly compensated by those associated to the description of the chlorine atom in the lhs.

Cl_2O isomers

Hydrochlorous acid, HOCl, is in equilibrium with its anhydride, Cl_2O, on the surface of ice crystals in the atmosphere [55], according to the already presented reaction (3). It is known to have C_{2v} symmetry and the experimental geometry was determined by microwave spectroscopy by Tanaka et al. [56] as r(OCl) = 1.69.587(7) Å and ∠ClOCl = 110.886(6) degrees. A second isomer, with the structure Cl-Cl=O, was observed spectroscopically already in 1967 by Rochkind and Pimentel [57] who determined two of the vibrational fundamentals (962-952 cm^{-1} and 368-377 cm^{-1}). The third one was determined by Chi and Andrews [58] in 1973 (241 cm^{-1}). The UV and IR spectra of this species were studied further by Johnsson et al [59] in 1995, who proposed that the formation occurred by geminal recombination of ClO and Cl, produced previously in the photolysis of the more stable isomer ClOCl. Later, a resonant Raman study of Cl_2O photochemistry in CCl_4 solution was performed by Esposito et al in 1999 [60]. Their results confirmed that photodissociation of Cl_2O produced ClO and Cl, followed by partial geminate recombination of those fragments, resulting in ClClO formation

The potential energy surface and the interconversion of the isomers has been studied several times, for instance by Collaveri et al [60], Grant et al [34], Xu and Lin [61] and An et al. [63]. The standard enthalpies of formation of both Cl_2O and ClClO at 298K are available experimentally. Thorn et al [64] determined a value of 18.44 ± 0.4 kcal/mol for ClOCl. Hassanzadeh and Irikura in 1997 revised the value of the enthalpy of formation of HOCl and obtained a slightly smaller value than the one used previously in this work, namely 17.9 ± 0.3 kcal/mol. Using eq. (3) they derived an experimental value of 19.4 ± 0.4 kcal/mol [65], 1 kcal/mol above the value of Thorn et al. On the other side, Chase reported the enthalpy of formation of ClClO as 22 ± 7 kcal/mol [33]. Using the usual composite methods in which CCSD(T) energies at lower levels are extrapolated to complete basis set level and several corrections for missing contributions are added, Matus et al [66] determined values of 18.9 kcal/mol and 31.9 kcal/mol for Cl_2O and ClClO respectively.

For the calculation of the enthalpy of formation in this work we will use the TAEs and the diatomic molecules as before

$$Cl_2O/ClClO \rightarrow 2Cl + O \qquad (9)$$

$Cl2O/ClClO \rightarrow Cl_2 + \frac{1}{2}O_2$ (10)

And the decompositions

$Cl_2O/ClClO \rightarrow ClO + Cl$ (11)

$Cl_2O/ClClO \rightarrow Cl_2 + O$ (12)

For the ClOCl species we will use also the isodesmic hydration reaction (3)

$H_2O(X^1A_1) + Cl_2O(X^1A_1) \rightarrow 2HOCl(X^1A')$ (3)

employing now the experimental enthalpy of formation of HOCl. Finally, we will also use the addition reactions

$Cl_2O/ClClO + O \rightarrow 2ClO$ (13)

$Cl_2O/ClClO + Cl \rightarrow Cl_2 + ClO$ (14)

In the case of ClClO, reaction (3) is not isodesmic and may lead to large errors. Instead of that, we used another reaction

$ClClO + HCl \rightarrow Cl_2 + HClO$ (15)

Reaction (15) is isodesmic, but we do not have an experimental value for the enthalpy of formation of HClO. We will use our best CCSD(T) value instead, 33.6 kcal/mol.

As we did previously with the other species, the error in the Cl-O bond length of the calculations at different levels with respect to the experimental value is shown in Fig. 10. The best value obtained at the CCSD(T)/aug-cc-pV6Z level differs in only 6×10^{-4} Å from the experimental one, similar to the error obtained in HClO (8×10^{-4} Å). With respect to the performance of the different methods there is no noticeable difference betwwen the results obtained for HOCl and ClOCl. Thus, the same considerations done previously apply in this case.

Similarly to what we did for HOCl, we show in Fig. 11 the CCSD(T) calculations of the enthalpy of formation of Cl_2O as obtained from the different reactions using the series of correlation consistent basis sets. Full lines show the convergence of the values obtained from reactions (3) and (10) which involve only closed shell species. The value obtained from reaction (10) at the CCSD(T)/aug-cc-pV6Z level is 18.45 kcal/mol, in excellent agreement with the experimental value of Thorn et al [64]. On the other side, the value obtained from the isodesmic reaction (3) at the same level is 19.17 kcal/mol, nearer to the value of Hassanzadeh and Irikura [65].

The dashed lines in Fig. 11 represent the convergence of the values obtained from reactions (9) and (11)-(14) which involve open shell species. The value obtained from the atomization reaction is 18.57 kcal/mol, also in agreement with Thorn et al [64] and lower than the theoretical value of Matus et al [66]. All the other reactions involving radicals give values near the experimental value of Thorn et al. Averaging the results of all the reactions (the black dotted line in Fig. 11) we find a value for $\Delta_f H^0_{298}$(Cl$_2$O) of 18.7 ± 0.5 kcal/mol within the error limits of both experimental determinations and in agreement to the theoretically derived value of Matus et al [66].

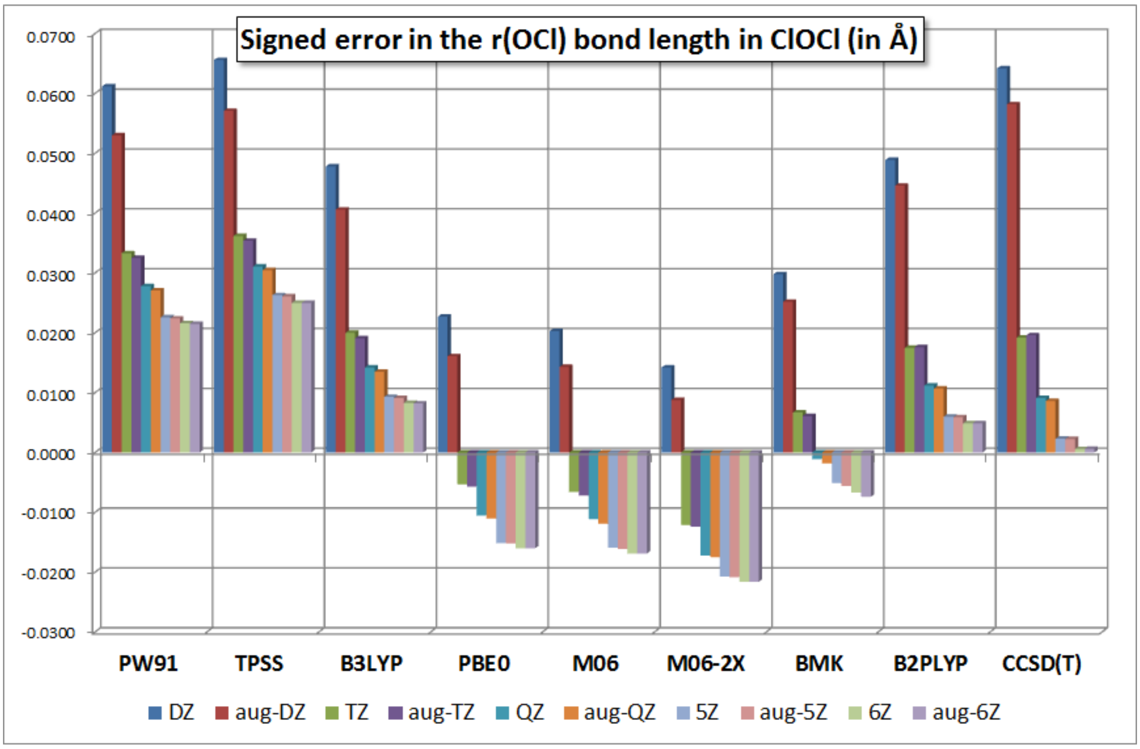


Figure 10. Signed error of the calculated r(ClO) bond length with respect to the experimental value (in Å) for each level of calculation

Table 5. Enthalpies of formation of ClOCl (in kcal/mol) obtained from reactions (3) and (9)-(14) using the indicated method and the aug-cc-pV6Z basis set. The average value of those obtained for all the reactions, as well as the standard deviation are shown in the last two columns of the table.

Method	(3)	(10)	(9)	(11)	(12)	(13)	(14)	Avg.	Std.Dev.
PW91	17.92	17.10	-2.00	15.79	5.21	33.58	23.00	15.80	11.57
TPSS	18.65	17.99	11.65	19.77	14.35	27.89	22.48	18.97	5.30
B3LYP	19.33	20.55	21.45	24.12	18.46	26.80	21.14	21.69	2.88
PBE0	19.95	21.87	18.24	22.04	19.44	25.84	23.24	21.54	2.57
M06	19.18	20.81	17.55	19.51	20.23	21.47	22.19	20.13	1.55
M06-2X	20.04	19.42	17.41	18.21	18.60	19.01	19.41	18.87	0.88
BMK	20.09	22.29	18.50	20.27	21.29	22.05	23.06	21.08	1.56
B2PLYP	18.90	20.10	19.51	20.70	17.86	21.90	19.06	19.72	1.32
CCSD(T)	19.17	18.45	18.57	18.53	18.73	18.49	18.69	18.66	0.24

The results obtained with the largest basis set used for all methods and reactions are collected in Table 5. It is clear that no DFT method can provide the same accuracy as CCSD(T) when employing a very large basis set. Of all the methods listed, M06-2X is the one that gives more similar results, in agreement with what we discussed previously. In the same line of thought as before, a combination of the M06-2X method with a not so large basis set (cc-pVQZ) give similar or better results than a CCSD(T) calculation with the same basis set. This can be appreciated, in the case of Cl_2O in the error distribution presented in the panels of Fig. 12.

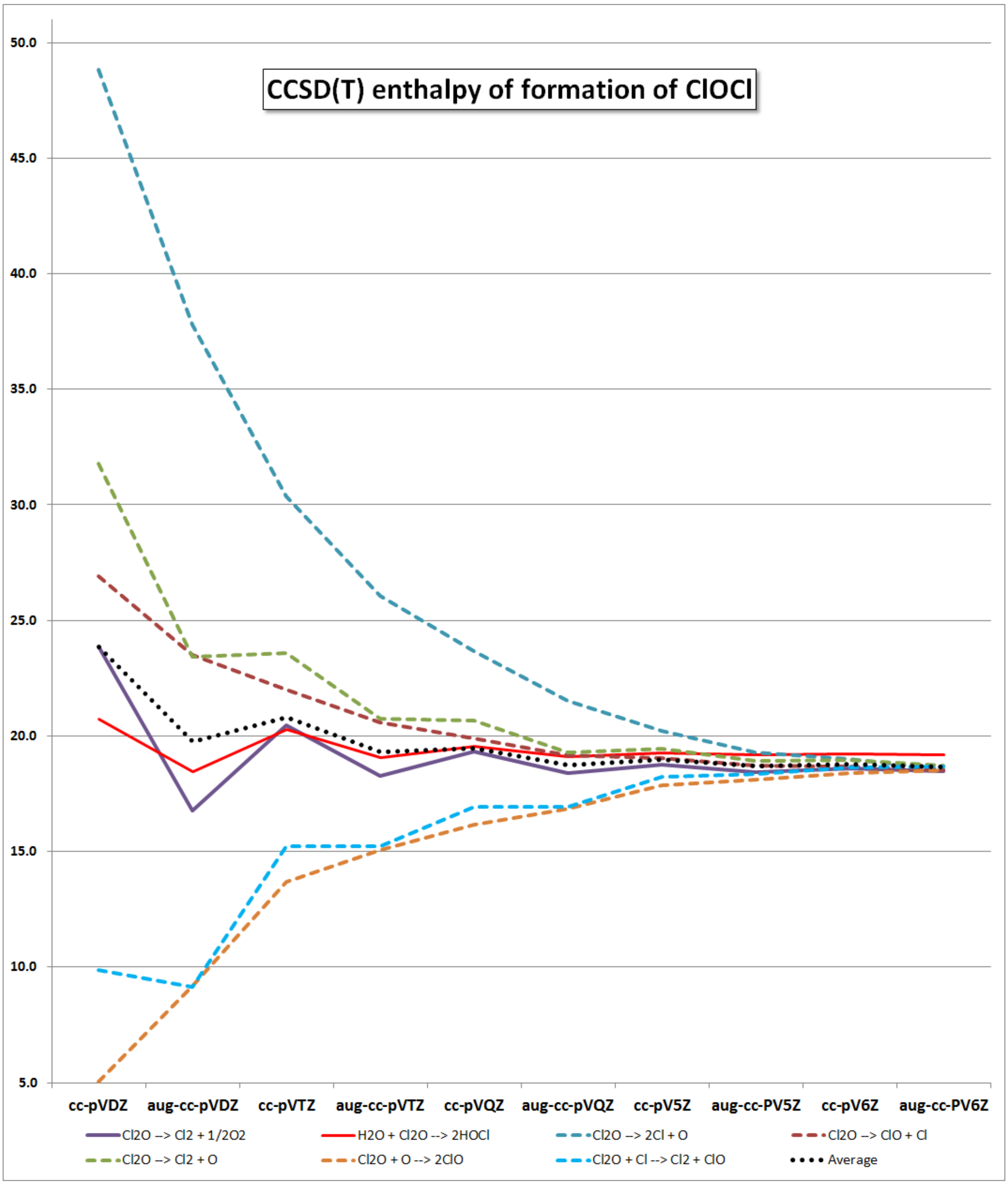


Figure 11. CCSD(T) calculation of the enthalpy of formation of Cl2O (in kcal/mol) using different basis sets and reactions. Full lines refer to reactions between closed-shell molecules. Dashed lines are the results for reactions involving radicals. The dotted black line is the average for all the reactions for each basis set.

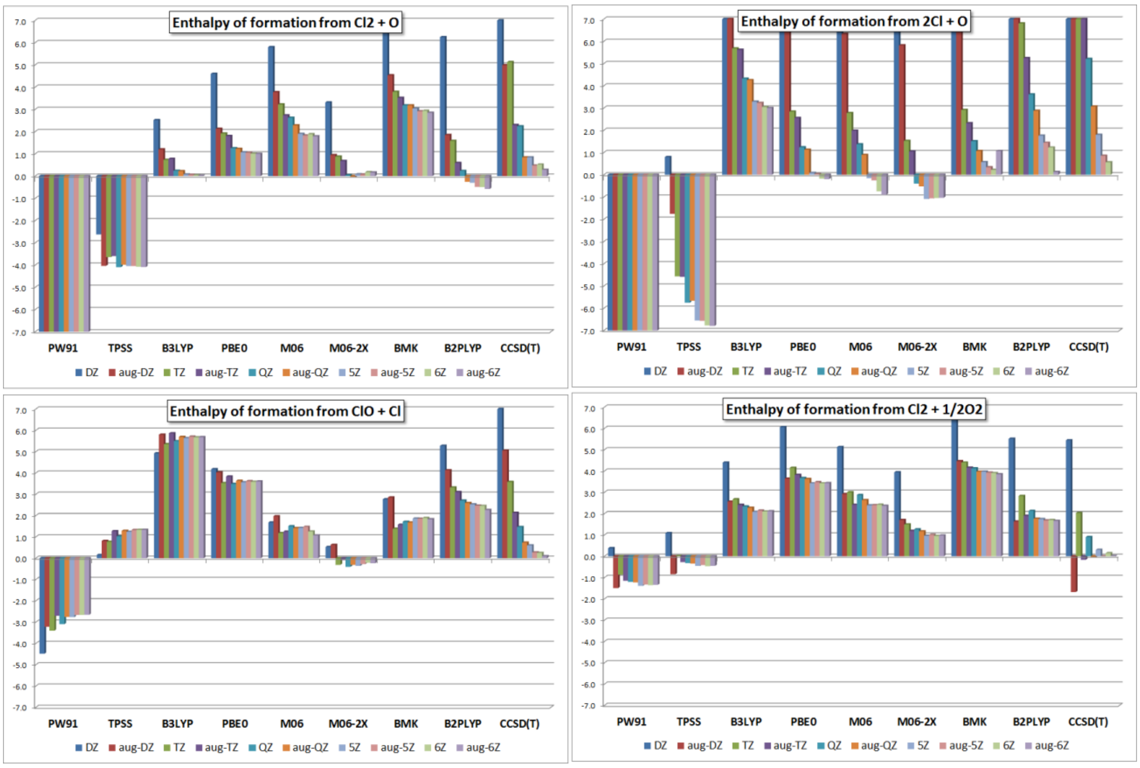


Figure 12. Signed error on the calculated enthalpies of formation (in kcal/mol) derived from different reactions using different methods and basis sets

In the case of ClClO we have no experimental data, except the rough estimation made by Chase, $\Delta_f H_{298}^0$(ClClO) = 22 ± 7 kcal/mol [33]. Therefore, we will assume that the CCSD(T) values have a similar accuracy than that show in the case of ClOCl. The convergence of the enthalpy of formation obtained from reactions (9) to (15) using the different correlation consistent basis sets is shown in Fig. 13. Reasonable convergence of all values is obtained for basis sets larger than cc-pV6Z and an average value of 32.1 ± 0.4 kcal/mol is obtained as a result, in agreement with the recommendation of Matus et al [66].

Table 6. Enthalpies of formation of ClClO (in kcal/mol) obtained from reactions (3) and (9)-(14) using the indicated method and the aug-cc-pV6Z basis set. The average value of those obtained for all the reactions, as well as the standard deviation are shown in the table.

Method	(9)	(10)	(11)	(12)	(13)	(14)	(15)	Avg.	Std.Dev.
PW91	3.81	22.91	21.60	11.03	39.39	28.82	28.26	22.26	11.83
TPSS	19.58	25.92	27.70	22.28	35.83	30.41	29.15	27.27	5.36
B3LYP	32.71	31.81	35.38	29.72	38.06	32.40	31.80	33.12	2.74
PBE0	28.23	31.86	32.03	29.43	35.83	33.23	32.60	31.89	2.49
M06	27.00	30.26	28.96	29.68	30.92	31.64	31.50	29.99	1.64
M06-2X/a6	34.26	36.27	35.06	35.46	35.87	36.26	36.45	35.66	0.79
M06-2X/Q	*36.72*	*38.38*	*36.71*	*37.15*	*36.70*	*37.14*	*35.88*	*36.95*	*0.76*
BMK	32.46	36.25	34.23	35.25	36.01	37.02	34.53	35.11	1.52
B2PLYP	31.23	31.82	32.42	29.58	33.62	30.78	31.72	31.60	1.27
CCSD(T)	32.01	31.90	31.97	32.17	31.94	32.13	32.46	32.08	0.19

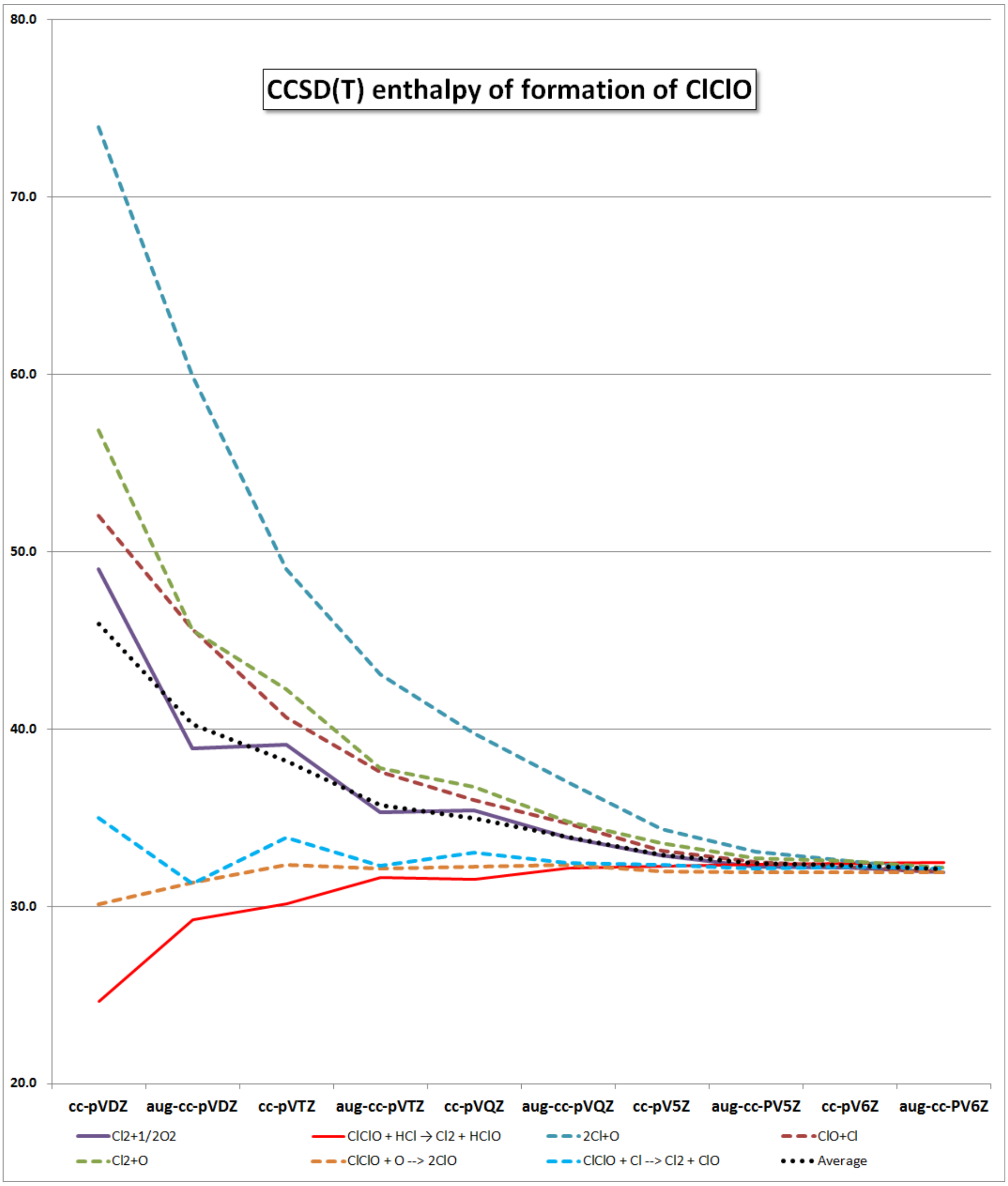


Figure 13. CCSD(T) calculation of the enthalpy of formation of ClClO (in kcal/mol) using different basis sets and reactions. Full lines refer to reactions between closed-shell molecules. Dashed lines are the results for reactions involving radicals. The dotted black line is the average for all the reactions for each basis set.

The enthalpies of formation obtained with the largest basis set are shown in Table 6. Similarly to the case of ClOCl, none of the DFT methods exhibit such a small dispersion as the CCSD(T) results. Moreover, the M06-2X method in this case, although exhibiting also the smallest dispersion of the DFT results, is not able to give a reasonably accurate result neither with the aug—cc-pV6Z or at the simpler cc-pVQZ level.

ClO_2 isomers

The last species studied in this paper are the radical isomers chlorine dioxide, OClO, and chlorine superoxide, ClOO. The most stable structure and the most important one from a practical point of view is the C_{2v} isomer OClO. This species is extensively used in pulp bleaching and in decontamination of drinkable water. The C_s chlorine superoxide, on the other side, presents some intriguing properties that make it a challenge for theoretical studies.

Very precise studies of the geometrical structure of these species exist. Chlorine dioxide has been experimentally known since the nineteenth century and well studied. Tanoura et al [67] studied the ground state rotational transitions of $^{35}ClO_2$ and $^{37}ClO_2$, while Miyazaki et al [68] studied the microwave spectra of $^{35}ClO_2$ and $^{37}ClO_2$ in the excited vibrational states, v_1, v_2, v_3, and $2v_2$, and determined the equilibrium structure of the OClO radical as r_e=1.46984 ± 0.00001 Å and ∠OClO=117.403 ± 0.003 degrees. The infrared and rotational spectra of this species—as well as that of the isomer—were studied for instance by Müller and Wilmer in 1993 [69] and Müller et al [70]. Theoretically, this species was studied several times, by Luke [71], Zhu and Lin [72], Karton et al [36], Peterson and Werner [73] [74] and Grant et al [34], among others. References to the latest experimental and theoretical work can be found in the recent work by Grein [75].

On the other side, chlorine superoxide has been a more elusive species. The existence of this radical was suggested as a reactive intermediate in the gas-phase photolysis reactions of Cl_2 with O_2 by Porter and Wright in the fifties [76]. Arkell and Schwager [77] in 1967 were the first to isolate the species in an Ar solid matrix and to determine its IR spectrum. In this paper there is already present some speculation about an intermediate ClOO* structure which would be responsible of some lines in the O-O stretching region. A theoretical discussion of the isomerization ClOO ↔ OClO, in solid matrices, implying the presence of an excited state $^2A'$—the ground state is $^2A''$—was presented by Gole in 1980 on the basis of Hartree-Fock calculations [78]. Müller and Wilner [69] compared the spectra of both isomers in Ne and Ar matrices, obtaining the superoxide by irradiation of the dioxide with visible light. Experimental geometric parameters for ClOO were determined as r_e(ClO)=2.139 Å, r_e(OO)=1.201 Å and ∠ClOO=115.7 degrees. Later experimental work was performed by Johnsson et al [79], who also observed ClOO* as a different species than ClOO, and by Thomsen et al [80]. The most recent experimental work on this radical was performed by Fourier transform infrared spectroscopy and FT microwave-millimeter wave double resonance spectroscopy by Suma et al [81], who found the parameters r_e(ClO)=2.084 ± 0.001 Å, r_e(OO)=1.206 ± 0.002 Å and ∠ClOO=115.4 ± 0.1 degrees.

From the thermochemical point of view, the most interesting topic is the relative stability of both isomers. This can be studied comparing directly their absolute energies or determining their respective enthalpies of formation resorting to these reactions

OClO / ClOO → Cl + O2 (½ Cl2 + O2) (16)

→ ClO + O (ClO + ½ O2) (17)

→ Cl + 2O (18)

In fact, while the asymmetrical chlorine superoxide seems to be thermodynamically more stable than chlorine dioxide, it is kinetically unstable and the study of this radical by high resolution spectroscopy in the gas phase has been currently unsuccessful, due probably to the decomposition as in reaction (16). Baer et al [82] studied the thermodynamic and kinetic properties of reaction (16) and determined that the bond dissociation energy was only 4.83 ± 0.05 kcal/mol. In contrast, the bond energy of the Cl-O bond in chlorine dioxide was found to be much higher, 55.2 ± 2.0 kcal/mol [83].

Other thermochemical property which we can obtain from reactions (16) to (18) are the enthalpies of formation of OClO and ClOO. Experimentally, the enthalpy of formation of OClO has been reported as 22.6 ± 0.3 kcal/mol by Sander et al [84] and as 23.53 ± 0.24 by Arkell and Schwager [77]. For ClOO, Wahner et al [85] determined a value of 23.4 ± 1.0 kcal/mol. The most recent and precise calculation of these values, done by Karton et al [35] at the W4 level [36], yielded values of $\Delta H_f^0(298K)$=23.9 kcal/mol for OClO and 25.1 kcal/mol for ClOO.

It is known that non-dynamical correlation is an important factor in the determination of the structure of these species [35]. Therefore, in this work we will discuss only the best results obtained for the bond energies and enthalpies of formation. A deeper analysis will be published elsewhere.

We show in Fig. 14 the convergence of the total energies (in Hartree) of the optimum geometries of ClOO and OClO at the CCSD(T) level with the correlation consistent and augmented correlation consistent basis sets. Two effects are immediately obvious. One is that both cc and aug-cc sets do converge slowly toward the CBS (complete basis set) limit. The second, that at the CCSD(T) level, OClO is less stable than ClOO, but the situation is reversed for large basis sets. This conclusion is reached also when the DFT methods are used. The convergence of the free energy difference with all methods shows a similar pattern, but two of them (B3LYP, BMK) predict ClOO to be more stable than OClO even with the larger basis sets. All the other methods, as well as CCSD(T), predict the inverse result, with a free energy difference between 1 and 5 kcal/mol (1.8 kcal/mol at the CCSD(T)/CBS level using Feller`s extrapolation method [86]).

We have collected in Table 7 the enthalpy differences between the isomers as well as the enthalpy of formation at room temperature obtained with all the methods employed in this paper. Only the results obtained with the larger basis sets are reported.

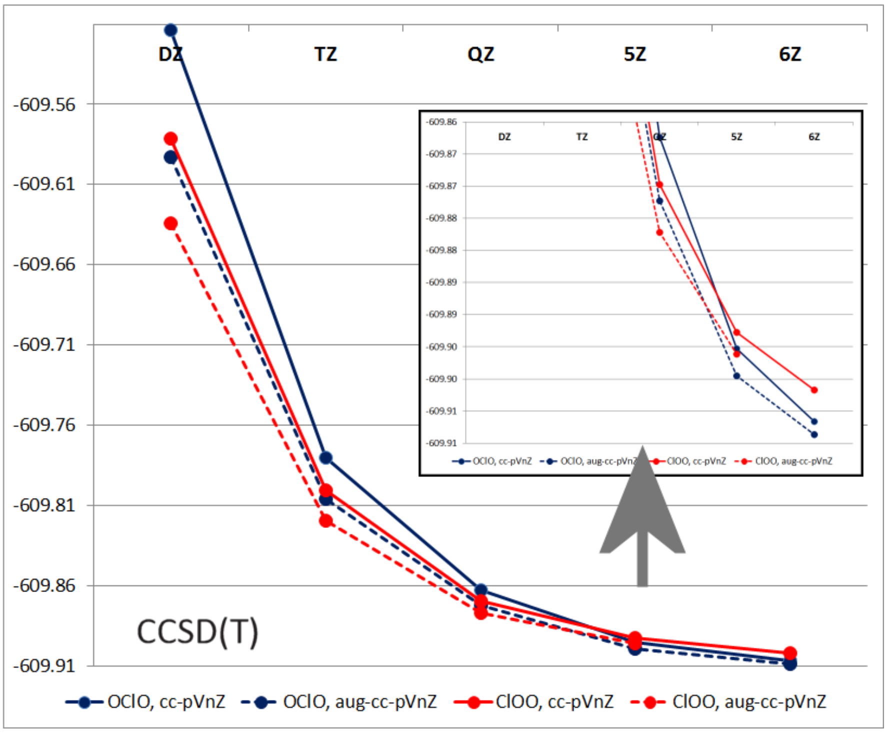


Figure 14. Total energies (in Hartree) for the isomers ClOO and OClO calculated at the CCSD(T) level employing cc and aug-cc basis sets. The inset shows an enlargment of the region of results with the larger basis sets.

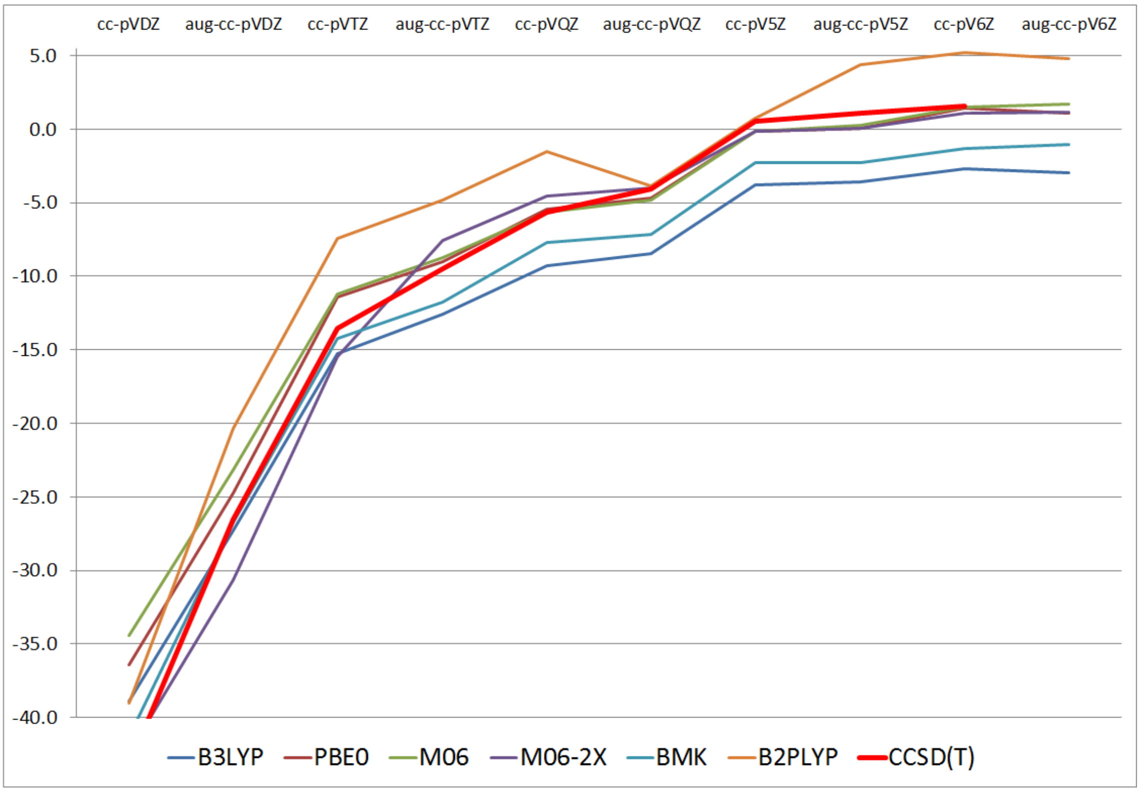


Figure 15. Free energy difference (in kcal/mol) between the ClOO and OClO isomers at their optimum geometries, calculated with several methods using cc and aug-cc basis sets.

Table 7. Relative energies (in kcal/mol) of the isomers of ClO2 and enthalpies of formation at room temperature determined from reactions (16) to (18)

Species	Method	Basis Set	$\Delta H(0)$	$\Delta H_f(298)$, Reac.16a	$\Delta H_f(298)$, Reac.16b	$\Delta H_f(298)$, Reac.17a	$\Delta H_f(298)$, Reac.17b	$\Delta H_f(298)$, Reac.18	Avg
ClOO	G4		2.99	28.1	28.1	26.2	26.1	27.6	27.2±1.8
	W1BD		4.50	28.3	29.1	27.2	27.7	27.8	28.1±1.1
	B3LYP	Aug6Z	-1.65	24.4	24.2	22.6	24.6	20.4	23.2±3.1
	PBE0	Aug6Z	2.41	24.6	26.4	23.2	25.5	19.9	23.9±4.5
	M06	Aug6Z	3.03	23.3	25.9	23.8	24.3	22.4	23.9±2.4
	M06-2X	Aug6Z	1.85	30.0	31.9	28.9	29.6	28.6	29.8±2.3
	BMK	Aug6Z	-0.26	27.5	30.2	27.0	27.9	25.7	27.7±2.9
	B2PLYP	Aug6Z	4.32	27.6	28.1	24.0	26.1	23.3	25.8±3.8
	CCSD(T)	6Z	2.46	25.5	26.8	25.7	25.2	26.5	25.9±1.2
	W4	CBS[1]	0.55						25.1
	Exper.[2]								23.4±1.0
OClO	G4			25.3	24.6	22.7	22.7	24.1	23.9±2.1
	W1BD			23.9	24.1	22.7	22.7	22.8	23.2±1.3
	B3LYP	Aug6Z		25.5	25.3	23.7	25.7	21.6	24.4±3.1
	PBE0	Aug6Z		21.7	23.5	20.3	22.6	17.0	21.0±4.5
	M06	Aug6Z		19.8	22.4	20.3	20.7	18.8	20.4±2.4
	M06-2X	Aug6Z		27.9	29.8	26.8	27.5	26.5	27.7±2.3
	BMK	Aug6Z		27.6	30.2	27.0	27.9	25.8	27.7±2.9
	B2PLYP	Aug6Z		22.4	22.8	18.8	20.9	18.1	20.6±3.8
	CCSD(T)	Aug6Z		22.4	23.7	22.6	22.2	23.1	22.8±1.1
	W4	CBS[1]							23.9
	Exper.[3]								22.6±0.3
	Exper.[4]								23.53±0.24

[1] Ref. [35] [2] Ref. [85] [3] Ref. [84] [4] Ref. [77]

Several observations can be done on these data. On the one side, that the agreement between the CCSD(T) results and the more recent experimental determinations of the enthalpy of formation is better for OClO than for ClOO. This is related to the difficulty in describing the Cl-O bond using monoconfigurational MO approaches. On the other side, one sees that the values obtained at the CCSD(T) level with the larger basis sets are very much in agreement with the W4 method which includes many more corrections and is a much more demanding procedure. It is also observed that neither for OClO nor for ClOO are the DFT methods able to give as accurate a result as the CCSD(T) method with the largest basis sets. We have estimated the precision of the calculations as $2*\sigma$ where σ is the standard deviation from the arithmetic mean of the results obtained for the enthalpy of formation from the five reactions (16) to (18). Both in terms of precision and accuracy, the CCSD(T) results are the only ones comparable to experiment. Notice that since the W4 uses atomization energies, the difference of enthalpies of formation between the isomers (1.2 kcal/mol) is about half the experimental one (2.5 kcal/mol). On the other side, the CCSD(T)/cc-pV6Z difference, as calculated in this work (i.e. geometry optimization performed as the same level than the calculations) afford a much nearer value (3.1 kcal/mol).

As we have observed in the other cases, DFT methods with smaller basis sets afford better results than when a large basis is used. In Fig. 16 we present the results for the series of basis sets and different functionals, as compared to the results obtained at the CCSD(T) level using the same basis sets.

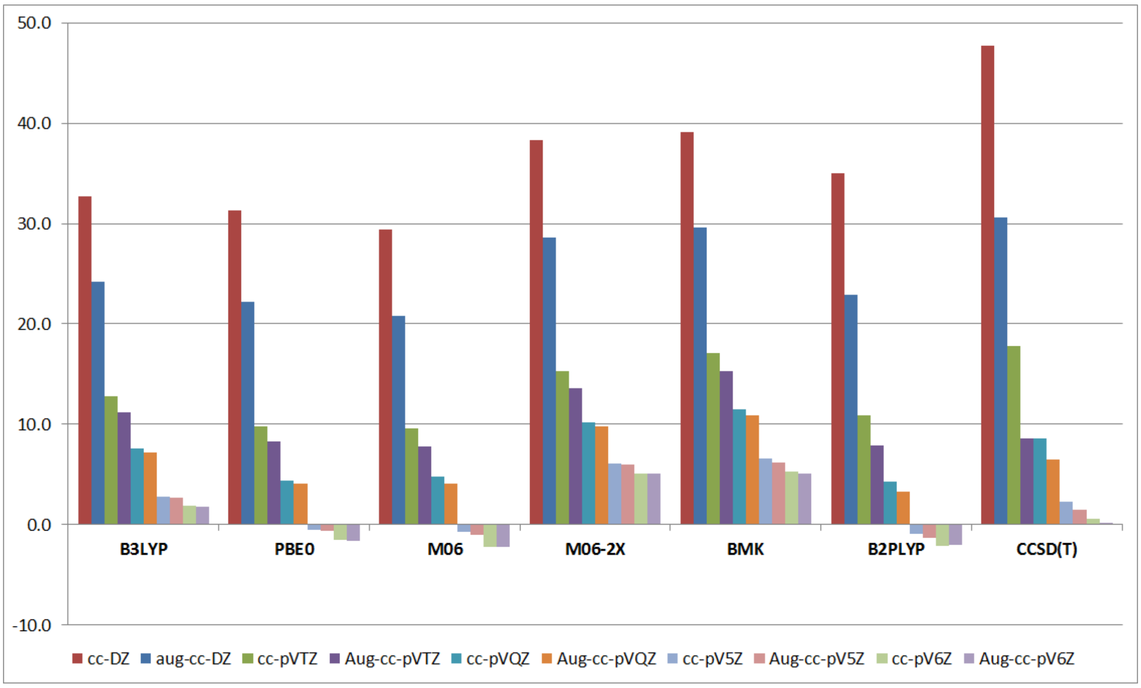


Figure 16. Unsigned error (with respecto to the experimental value) in the enthalpy of formation of OClO at 298.15K (in kcal/mol) as compared to the CCSD(T) calculations with the cc and aug-cc basis sets

We observe again that the error in some of the DFT calculations change sign with the increase of the basis set. Thus, there is an error compensation between the potential and the basis set, although this is not the case for all methods. One important point however, is that when a small basis set is used (anything smaller than aug-cc-pV5Z) almost all DFT calculations give a smaller error than the CCSD(T) calculations. In all cases the error is unacceptably large (more than 5 kcal/mol) but it is larger with CCSD(T) methods. With a carefully selected choice of method and basis sets (M06 or B2PLYP with the cc-pV5Z basis set, for instance) the error is less than 1 kcal/mol, an error obtainable at the CCSD(T) level only if basis cc-pV6Z or aug-cc-pV6Z are used. Needless to say, the latter calculations are much slower and more demanding than the DFT ones.

Conclusions

MP2, CCSD(T), density functional and composite chemical methods were employed in this paper to study the ClO radical species as well as the two isomeric structures XClO/ClOX for each X=H, Cl and O.

The main purpose of the study was to compare the performance of several DFT methods (PW91, TPSS, B3LYP, PBE0, M06, M06-2X, BMK and B2PLYP) to describe the Cl-O bond is radicals important in atmospheric chemistry. Geometry optimizations as well as reaction enthalpies and enthalpies of formation for each species were calculated using Pople basis sets and the (aug)-cc-pVnZ Dunning sets, with n=2-6. For the calculation of enthalpies of formation, atomization as well as isodesmic reactions were employed.

Both the precision of the methods with respect to the increase of the basis sets, as well as their accuracy, were estimated by comparing the results with the more accurate CCSD(T) calculations, performed using the same basis sets as for the DFT methods. The results obtained employing composite chemical methods (G4, CBS-QB3 and W1BD) were also used for the comparisons, as well as experimental data when it was available.

The results obtained show that error compensation is the key for successful description of molecular properties (geometries and energies) by carefully selecting the method and the basis set. In general, expansion of the one-electron basis set to the limit of completeness does not improve results at the DFT level—as it occurs with precise post-Hartree-Fock MO methods—but just the opposite. The enthalpies of formation calculated at the CCSD(T)/aug-cc-pV6Z for the species considered are generally in agreement with experimental determinations, and the most accurate derived theoretically up to present. In the case of the DFT methods we found that a reasonable description of the Cl-O bond across the species studies can be obtained at the M06/aug-cc-pVQZ or M06/cc-pV5Z. Other methods can occasionaly produce better results but are not generally as accurate in all cases.

Acknowledgments

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