

# Structure and Bonding of Chlorine Oxides and Peroxides: $\text{ClO}_x$ , $\text{ClO}_x^-$ ( $x = 1-4$ ), and $\text{Cl}_2\text{O}_x$ ( $x = 1-8$ )

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The structural and bonding properties of the chlorine oxides and peroxides  $\text{ClO}_x$ ,  $\text{ClO}_x^-$ , ( $x = 1-4$ ) and  $\text{Cl}_2\text{O}_x$  ( $x = 1-8$ ) in their ground state have been investigated with the hybrid spin unrestricted and spin restricted Hartree–Fock density functional method. The equilibrium structures of the most stable isomers in each stoichiometry have been determined. It is found that the di-chlorine oxides avoid the formation of a Cl–Cl bond, and therefore have either an oxo or peroxy structure. The calculated vibrational harmonic frequencies are in good agreement with the available gas phase or matrix isolation IR data. The calculated adiabatic electron affinities of the mono-chlorine species are, respectively, 2.23, 2.14, 4.07, and 5.1 eV for  $\text{ClO}$ ,  $\text{ClO}_2$ ,  $\text{ClO}_3$ , and  $\text{ClO}_4$ . The reaction enthalpies of the possible channels leading to the formation of di-chlorine oxides and peroxides  $\text{Cl}_2\text{O}_x$  from mono-chlorine oxide fragments are reported and discussed. A comparative discussion of the bonding in these species has been carried out on the basis of the topological analysis of the electron localization function (ELF). It is found that the odd electron of the mono-chlorine species is distributed on the oxygen and chlorine lone pairs. The weak populations of the ClO bond basins and the absence of spin density within them leads to discarding a picture in which three electrons are involved in the ClO bond. The localization of the spin density in the mono-chlorine oxides determines the reactive center: oxygen for  $\text{ClO}$  and  $\text{ClO}_4$ , chlorine for  $\text{ClO}_2$  and  $\text{ClO}_3$ . The formation of the di-chlorine oxides and peroxides from the mono-chlorinated species follows the two following rules: (i) the formation of a Cl–Cl bond never yields the most stable isomer, (ii) the chemical bond linking the two fragments is formed between their reactive centers provided rule (i) is satisfied.

## 1. Introduction

The oxides and peroxides of chlorine have raised a broad interest in recent years because of their importance in the upper atmosphere chemistry<sup>1–8</sup> and particularly as intermediates and precursors occurring in the chlorine photosensitized decomposition of ozone. Though the most stable members have been known for more than 150 years,<sup>9</sup> there has been evidence of rather unstable radicals since the late sixties with the development of the matrix isolation spectroscopy.<sup>10–12</sup> The mono-chlorine oxides are very reactive radicals, often short-lived and therefore difficult to observe. The di-chlorine oxides are also very unstable, for example  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2\text{O}_3$  are explosive whereas  $\text{Cl}_2\text{O}_4$  and  $\text{Cl}_2\text{O}_6$  decompose at room temperature.<sup>9</sup> Little is known about their structures from experiment. The possible combination reactions of the  $\text{ClO}_x$  radicals have been investigated by Colussi and Grela<sup>13</sup> on the ground of a valence bond additivity scheme. These authors predicted the unobserved  $\text{ClO}_3\text{–O–ClO}_3$  and  $\text{ClO}_3\text{–O–O–ClO}_3$  peroxides to be relatively stable. Cl–O–ClO<sub>3</sub> and ClO<sub>3</sub>O–ClO<sub>3</sub> species involve one bridging oxygen, and are, respectively, pale yellow and colorless liquids. The structure of  $\text{Cl}_2\text{O}_6$  is either Cl–Cl linked or oxygen-bridged.

Quantum chemical calculations offer an alternative to search unknown species and enables rather reliable determinations of

their structure, heat of formation, and electron affinities.<sup>14–22</sup> Up to now, the largest system investigated by ab initio methods is  $\text{Cl}_2\text{O}_3$ .<sup>22</sup> From a technical viewpoint, the most recent calculations have shown that reliable results are obtained with the hybrid Hartree–Fock/density functional approach of Becke<sup>23</sup> provided a sufficient basis set is used.<sup>21,22</sup>

The nature of the chemical bond in the chlorine oxides and peroxides has not held much attention. It is commonly assumed that terminal oxygens form dative bonds with chlorine whereas bridging-oxygen–chlorine bonds are covalent. Though  $\text{ClO}_2$  is discussed in detail in Pauling's classical textbook<sup>24</sup> as prototype of the three-electron bond, only a few recent papers have been devoted to this topic, we can mention the work of Harcourt on the valence bond structures of  $\text{ClO}_2$  and of its dimer.<sup>17</sup> Particularly, the localization of the odd electron of the radical species which can be a clue to understanding their reactivity has not been investigated enough.

The aim of the present paper is to present a state of the art quantum chemical investigation of the mono-chlorine and di-chlorine oxides and peroxides in order to determine the structure and the vibrational properties of the stable isomers or conformers, to understand their reactivity, and to investigate the nature of the bonding.

## 2. Computational Method

The ab initio calculations have been performed at the hybrid Hartree–Fock density functional level B3LYP<sup>23,25–27</sup> with the

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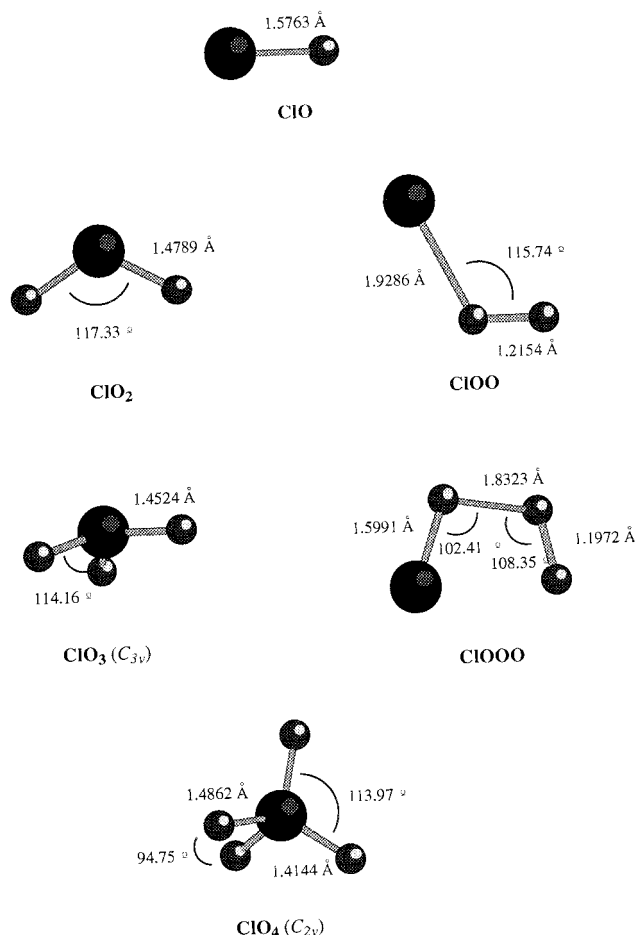
Gaussian94 software.<sup>28</sup> The reliability of the B3LYP scheme is well established for the prediction of structure, heat of formation, and vibrational properties of molecules.<sup>29–32</sup> In the particular case of  $\text{Cl}_2\text{O}_3$ , Clark and Francisco<sup>22</sup> have demonstrated that B3LYP/6-311+G(3df) calculations yield very accurate values of the enthalpy and entropy of formation. The optimization of the structural parameters of the di-chlorine molecules has been carried out in two steps in order to lower the computational effort. The internal coordinates of the  $\text{Cl}_2\text{O}_x$  species have a rather large degree of freedom, and it is therefore necessary to explore all the structural possibilities. The search of the most stable isomers in each stoichiometry has been done therefore with a light basis set, i.e., 6-31G(d).<sup>33–35</sup> As this basis set tends to noticeably overestimate the bond lengths with respect to experiments, a noticeable improvement in the optimized structures, relative energies, and calculated frequencies can be achieved with a better basis set such as the 6-311+G(3df)<sup>34–37</sup> basis set. Starting from the 6-31G(d) structures, the geometry of each compound has been optimized with the large basis set and the vibrational frequencies and zero-point energy corrections calculated. The discussion of the bonding relies on the topological analysis of the ELF function. This analysis has been carried out with the ToPMoD program developed at the Laboratoire de Chimie Théorique de l'Université Pierre et Marie Curie.<sup>38</sup>

An illustration of the reliability of the B3LYP/6-311+G(3df) scheme is provided by the calculated values of the equilibrium internuclear distances  $r_e$ , harmonic stretching frequencies  $\omega_e$ , and dissociation energies  $D_e$  of the dioxygen and di-chlorine molecules in their ground states. The experimental values<sup>39</sup> being given in parenthesis, one finds  $r_e = 1.203$  (1.207) Å,  $\omega_e = 1644.6$  (1580.36)  $\text{cm}^{-1}$ , and  $D_e = 5.27$  (5.08) eV for  $\text{O}_2$  ( $^3\Sigma_g^-$ ), and  $r_e = 2.010$  (1.988) Å,  $\omega_e = 540.9$  (564.9)  $\text{cm}^{-1}$ ,  $D_e = 2.54$  (2.475) eV for  $\text{Cl}_2$  ( $^1\Sigma_g^+$ ).

### 3. Results and Discussion

The mono-chlorine oxides  $\text{ClO}_x$  ( $x = 1–4$ ) are doublets in their ground state whereas the di-chlorine oxides  $\text{Cl}_2\text{O}_x$  ( $x = 1–8$ ) are closed-shell singlets. Most of these latter systems can be viewed as dimers and codimers of the mono-chlorine oxides. The results of the structure optimizations carried out with the 6-311+G(3df) basis are given in Figures 1, 2, and 3. The total electronic energies of the different compounds are given in Table 1. The available experimental structures have been determined from the rotational spectra of  $\text{ClO}$ ,<sup>40</sup>  $\text{ClO}_2$ ,<sup>41</sup>  $\text{Cl}_2\text{O}$ ,<sup>42</sup>  $\text{Cl}_2\text{O}_2$ ,<sup>43</sup> and  $\text{Cl}_2\text{O}_3$ ,<sup>44</sup> estimated from force constant–bond length empirical relations for  $\text{ClOO}^{11}$  and  $\text{ClO}_3$ <sup>45</sup> or refined from the X-ray diffraction patterns for  $\text{Cl}_2\text{O}_6$ .<sup>46,47</sup> The comparison between calculated and experimental values is therefore restricted to the first group of molecules since noticeable distortions from the isolated molecule structure are expected to occur in the crystalline phases. The frequencies calculated at the harmonic level of the molecules for which the experimental vibrational spectrum has been reported in the literature are presented in Tables 2 and 3, the frequencies and intensities of the remaining molecules are provided in Table 3S as supporting information.

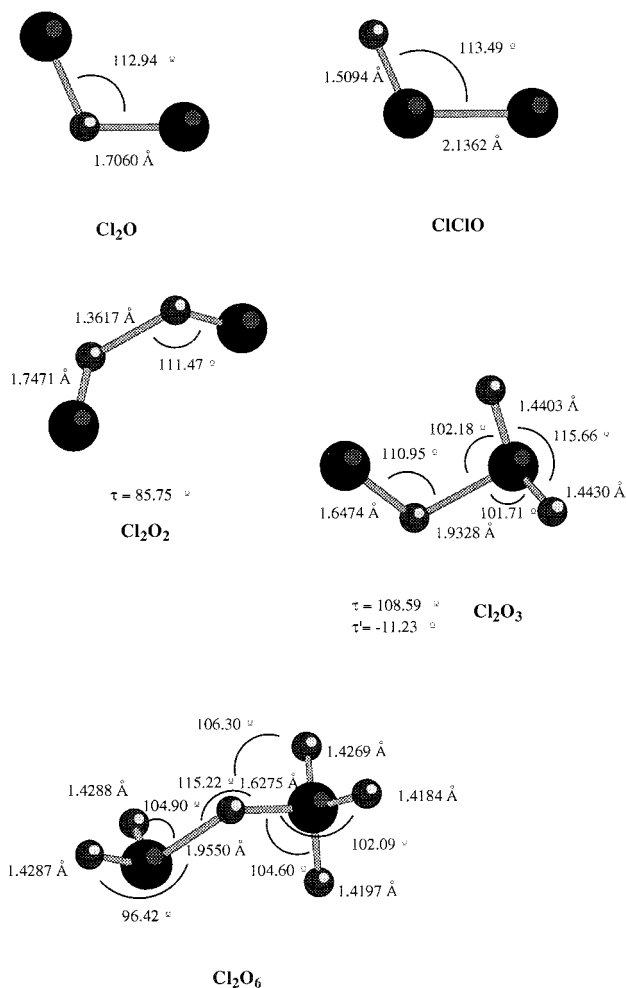
**3.1. Mono-Chlorine Oxides  $\text{ClO}_x$ .** The systems considered are  $\text{ClO}$ , the two isomers with  $\text{ClO}_2$  stoichiometry [the chlorine dioxide,  $\text{OClO}$  of ( $C_{2v}$ ) and peroxide  $\text{ClOO}$  ( $C_s$ )], the two isomers of the chlorine trioxide [namely,  $\text{ClO}_3$  ( $C_{3v}$ ) and  $\text{ClOOO}$  ( $C_s$ )], and the chlorine tetraoxide  $\text{ClO}_4$  radical in the  $T_d$ ,  $C_{3v}$ , and  $C_{2v}$  symmetries. As the mono-chlorine oxides and peroxides are open-shell systems, the optimization of the structural parameters has been carried out within both spin-unrestricted and spin-restricted schemes. For  $\text{ClO}$ ,  $\text{OClO}$ ,  $\text{ClO}_3$  ( $C_{3v}$ ), and  $\text{ClO}_4$  the



**Figure 1.** Optimized structures of the oxides  $\text{ClO}_x$ .

two approaches yield identical equilibrium structures, whereas noticeable differences are observed for  $\text{ClOO}$  and  $\text{ClOOO}$ . Though analytical second derivatives of the energy are only available at the spin-unrestricted level, the frequency calculations have been duplicated at the spin-restricted level, the two methods yielding sometimes rather different frequency values. The mono-chlorine oxides have been the subject of many experimental<sup>11,40,48,49</sup> as well as theoretical studies.<sup>15–18,20,50–53</sup> However, only a few DFT studies have been published so far.<sup>50,51</sup> The chlorine monoxide,  $\text{ClO}$ , is well described by DFT results: the theoretical value of the  $\text{Cl–O}$  distance and the stretching harmonic frequency are both in agreement with experimental data<sup>40,42</sup> and previous theoretical results.<sup>50</sup> The bond length is calculated larger than the experimental one by only 0.007 Å. The harmonic frequency  $\omega_e(\text{ClO})$  is correctly predicted by the spin restricted calculation,  $\omega_e = 861.1$   $\text{cm}^{-1}$  (866 experimentally) whereas it is underestimated by about 40  $\text{cm}^{-1}$  by the spin-unrestricted approximation although the two optimized internuclear distances are identical.

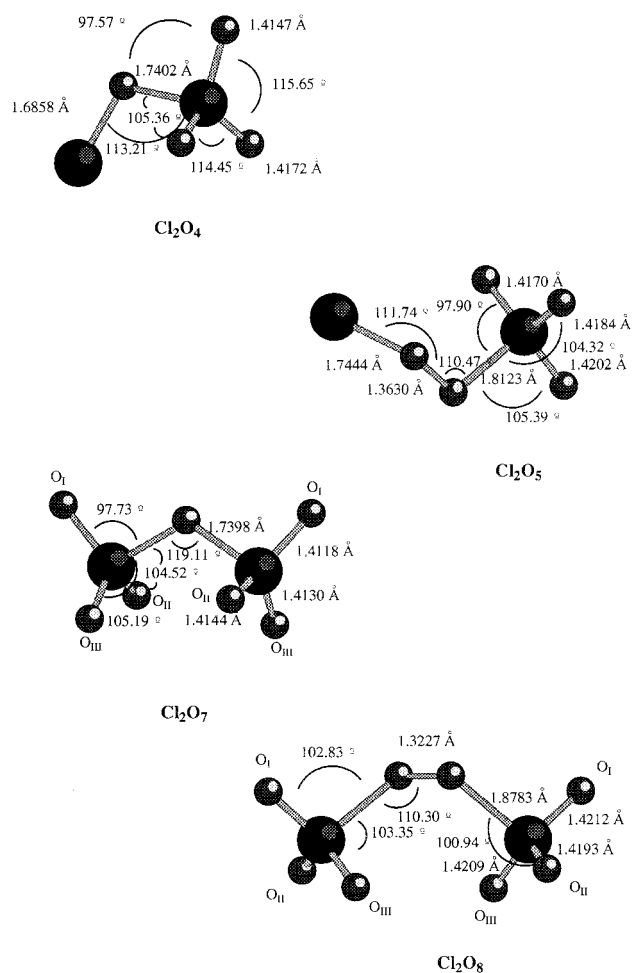
The chlorine dioxide has been extensively experimentally<sup>11,41,48,54</sup> and theoretically<sup>15–17,20,49–53</sup> studied, probably because of its industrial interest. There are two isomers which have both been studied by spectroscopic techniques. The  $C_{2v}$  isomer,  $\text{OClO}$ , has been characterized by many high-resolution spectroscopic methods including microwave spectroscopy, while the peroxo-like  $\text{ClOO}$  isomer has been observed predominantly by matrix isolation methods.  $\text{ClOO}$  is thermodynamically more stable than  $\text{OClO}$  by about 4 kcal/mol. This value is derived from the difference between the two dissociation energies  $D_e$  ( $\text{OClO} \rightarrow \text{O}_2 + \text{Cl}$ ) and  $D_e$  ( $\text{ClO}_2 \rightarrow \text{O}_2 + \text{Cl}$ ).<sup>16</sup> The value 2.45 kcal/mol calculated in the present work agrees with the



**Figure 2.** Optimized structures of the oxides  $\text{Cl}_2\text{O}_x$ . The complete set of geometrical parameters can be obtained from the authors.

experimental estimate and with previous theoretical values based on the extensive ab initio calculations of Lee et al.<sup>53</sup> For the  $C_{2v}$  isomer the spin-unrestricted and spin-restricted calculations yield almost identical optimized structures and vibrational frequencies which are in excellent agreement with the available experimental data<sup>41,54</sup> as well as with previous quantum chemical calculations.<sup>16,50,51</sup> The calculated structural parameters and vibrational frequencies of the ClOO isomer appear to be rather sensitive to the open-shell scheme: the ClO distance is calculated larger with the spin-unrestricted approximation (2.257 Å) than with the spin-restricted method (1.929 Å), whereas the OO distance behaves in the opposite way (1.193 and 1.215 Å, respectively). As a consequence, the OO stretching frequency is overestimated by the ROB3LYP scheme and underestimated by UB3LYP while the opposite trends are observed for the ClO stretching and ClOO bending frequencies. Incidentally, the observed<sup>11,54,55</sup> and post Hartree–Fock values<sup>16</sup> are between the two sets.

The structural parameters and vibrational frequencies calculated for the  $C_{3v}$  isomer of  $\text{ClO}_3$  are in very good agreement with previous calculations<sup>18,50</sup> and with the experimental IR spectrum.<sup>45</sup> The energy of this molecule is 30 kcal/mol higher than the sum of the energies calculated for ClO and  $\text{O}_2$ ; therefore, one can expect that the ClOOO isomer is more stable than the  $C_{3v}$  isomer. However, the stability of this isomer remains an open question. On one hand Rauk et al.<sup>18</sup> found it unstable, though lower in energy than the  $C_{3v}$  isomer, on the basis of RMP2 and QCISD(T) calculations, on the other hand



**Figure 3.** Optimized structures of the oxides  $\text{Cl}_2\text{O}_x$  (continued). The complete set of geometrical parameters can be obtained from the authors.

**TABLE 1: Total Electronic Energies and Zero-Point Corrected Energies (in hartree) of  $\text{Cl}_x\text{O}_y$  species Calculated at the Spin-Restricted B3LYP/6-311+G(3df,2p) Level**

$\text{Cl}_x\text{O}_y$ compound	electronic energy	ZPE corrected energy}
ClO	-535.362784	-535.360822
ClO	-610.547285	-610.541500
ClOO	-610.550547	-610.545413
$\text{ClO}_3$ ( $C_{3v}$ )	-685.695245	-685.684692
ClOOO	-685.728184	-685.719563
$\text{ClO}_4$ ( $C_{2v}$ )	-760.853660	-760.839579
$\text{Cl}_2\text{O}$ ( $C_{2v}$ )	-995.582531	-995.578881
ClClO	-995.562944	-995.559197
$\text{Cl}_2\text{O}_2$ (ClOO Cl)	-1070.751652	-1070.744978
$\text{Cl}_2\text{O}_3$ (Cl'OCi(O')O'')	-1145.927160	-1145.916010
$\text{Cl}_2\text{O}_4$ (ClOCl'O <sub>3</sub> )	-1221.094390	-1221.077202
$\text{Cl}_2\text{O}_5$ (ClOOCl'O <sub>3</sub> )	-1296.257571	-1296.237797
$\text{Cl}_2\text{O}_6$ ( $\text{O}_2\text{ClOCl}'\text{O}_3$ )	-1371.432650	-1371.407968
$\text{Cl}_2\text{O}_7$ ( $\text{O}_3\text{ClOCl}'\text{O}_3$ )	-1446.594915	-1446.564623
$\text{Cl}_2\text{O}_8$ ( $\text{O}_3\text{ClOOCl}'\text{O}_3$ )	-1521.763622	-1521.731149

the B3LYP calculation of Janoschek<sup>50</sup> concludes to its stability. In our case the geometry optimization converges toward a set of parameters very close to those published by Janoschek,<sup>50</sup> with both UB3LYP and ROB3LYP. The latter open-shell scheme yields a set of real positive frequencies whereas there is one imaginary frequency with the spin-unrestricted approximation. The optimized  $C_s$  structure is nonetheless a true minimum even at the unrestricted level, we think that an artifact due to a spin contamination effect on the energy derivatives should be at the origin of the imaginary frequency. The energy of this isomer is

**TABLE 2: Calculated Harmonic ( $\omega$ ) and Experimental Anharmonic ( $\nu$ ) Vibrational Frequencies ( $\text{cm}^{-1}$ )**

ClO <sub>x</sub> compound	assignment	$\omega$ (calcd)		$\nu$ (expt)
		UB3LYP	ROB3LYP	
ClO				[42]
	str.	826.1	861.1	866
OCIO				[54]
	Cl–O a. str.	1119.6	1120.3	1107.6
	Cl–O s. str.	968.2	968.0	944.8
	O–Cl–O bend.	451.3	451.2	448.7
CIOO				[54] [55]
	O–O str.	1595.8	1397.1	1477.8 1442.8
	Cl–O–O bend.	325.1	548.9	432.4 408.3
	O–Cl str.	109.4	307.5	214.8 192.4
ClO <sub>3</sub> ( <i>C<sub>3v</sub></i> )				[45]
	Cl–O a. str.	1081.2	1095.5	1081.27
	Cl–O s. str.	923.5	929.8	905.04
	s. bend.	563.9	565.6	566.63
	a. bend.	471.8	473.0	475.76
CIOO'O'				<i>i</i>
	O–O' breathing	1540.4	1540.2	
	Cl–O str.	820.8	842.9	
	OO'O'' bend.	545.6	578.8	
	a. bend.	206.8	380.3	
	rock.	189.6	242.2	
	O–O' str.	imaginary	199.8	
ClO <sub>4</sub> ( <i>C<sub>2v</sub></i> )				[12]
	<i>b<sub>2</sub></i> str.	1256.7	1253.2	1234
	<i>a<sub>1</sub></i> str.	1160.2	1158.2	1161
	<i>a<sub>1</sub></i> str.	903.6	908.0	874
	<i>b<sub>1</sub></i> str.	647.7	634.2	646
	<i>a<sub>1</sub></i> bend.	572.3	572.2	576
	<i>b<sub>2</sub></i> bend.	549.7	550.5	
	<i>b<sub>1</sub></i> rock.	412.5	383.0	
	<i>a<sub>1</sub></i> rock.	385.4	374.4	
	<i>a<sub>1</sub></i> twist.	375.3	347.2	

calculated above the dissociation limit by only 8 kcal/mol, it is therefore lower in energy than the *C<sub>3v</sub>* isomer by 22 kcal/mol.

Unlike the previous mono-chlorine oxide compounds, the experimental structure of ClO<sub>4</sub> radical, an important intermediate in reactions involving ozone, is not clearly proved. Therefore, this system will be studied in more detail. A first series of calculations has been performed on the ClO<sub>3</sub>F molecule in order to get an additional benchmark of the reliability of the optimized geometry and calculated frequencies. The choice of this molecule is justified by its close relationship with ClO<sub>4</sub> and by the availability of accurate experimental data. The optimized structural parameters and vibrational frequencies of ClO<sub>3</sub>F are reported in Table 4 along with the corresponding experimental values. The only stable ground-state structure is found to belong to the *C<sub>2v</sub>* point group. It corresponds to a <sup>2</sup>B<sub>2</sub> electronic state and its energy is higher than the dissociative limit into ClO<sub>2</sub> + O<sub>2</sub> by 45.7 kcal/mol. Moreover, geometry optimizations carried out with higher symmetry group (namely *C<sub>3v</sub>* and *T<sub>d</sub>*) constraints yield saddle point of index one in the potential energy surface. The *C<sub>2v</sub>* structure lies  $5.10 \times 10^{-3}$  au (3.1 kcal/mol) below the *C<sub>3v</sub>* structure, whereas the energy difference with respect to the *T<sub>d</sub>* saddle point is larger ( $1 \times 10^{-2}$  au = (6.3 kcal/mol)). As the chlorine atom is coordinated to oxygen atoms only two *C<sub>2v</sub>* equivalent structures are possible which are connected by the *C<sub>3v</sub>* and *T<sub>d</sub>* saddle point according to the number of Cl–O bonds which are shortened/lengthened by pseudorotation. The difference between the two bond lengths is about 0.07 Å, while the two non equivalent bond angles differ by about 20. We can notice that the value of these variables found for the ClO<sub>4</sub><sup>−</sup> anion is intermediate,<sup>21</sup> the energy minimum being close to the saddle point values and the ClO<sub>4</sub> radical appears to be a floppy molecule.

The harmonic frequencies and intensities of the vibrational lines of <sup>35</sup>Cl<sup>16</sup>O<sub>4</sub> and <sup>35</sup>Cl<sup>18</sup>O<sub>4</sub> isotopic species have been

**TABLE 3: Calculated Harmonic ( $\omega$ ) and Experimental Anharmonic ( $\nu$ ) Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Di-Chlorine Oxides<sup>a</sup>**

Cl <sub>2</sub> O <sub>x</sub> compound	assignment	$\omega$ (calcd)		$\nu$ (expt)	
ClOCl				[64]	
	OCl a. str.	654.46		686	
	OCl s. str.	651.70		640	
	Cl–O–Cl bend.	295.75		300	
ClClO				[110]	
	OCl str.	986.18		962	
	ClCl str.	406.92		375	
	ClClO bend.	295.75		239	
Cl <sub>2</sub> O <sub>2</sub> (ClOOCl)				[71]	
	OO str.	844.36		754.0	
	ClO a. str.	640.54		647.7	
	ClO s. str.	553.69		543.0	
	CIOO a. bend.	442.82		418.5	
	CIOO a. bend.	327.16		310	
	torsion	121.03		114	
Cl <sub>2</sub> O <sub>3</sub> (Cl'OCi(O')O'')			[72]		[73]
	ClO' a. str.	1232.74	1226.1	1225	
	ClO' s. str.	1062.36	1058.4	1057	
	ClO' str.	763.81	730.9	740	
	O'ClO bend.	539.04	565.4	560	
	O'ClO'' rock	433.03			
	ClO str.	367.82			
	OCIO' bend.	255.19			
	OCIO'' bend.	186.12			
	ClOCl' torsion	54.41			
Cl <sub>2</sub> O <sub>6</sub> (O <sub>i,j,m</sub> ) <sub>3</sub> ClOCl'(O'' <sub>i,j,m</sub> ) <sub>3</sub>				$\nu$ (expt) [74]	
				Ne	Ar
	as. str. Cl'OO'' <sub>3</sub> + ClO <sub>2</sub>	1284.58	1284.1	1284.1	
	as. str. Cl'OO'' <sub>3</sub> + ClO <sub>2</sub>	1263.39	1263.1		1265.0
	as. str. Cl'O'' <sub>3</sub>	1242.37	1249.5	1249.5	
	s. str. Cl'O'' <sub>3</sub>	1102.75	1082.3	1081.5	1080
	s. str. Cl'O'' <sub>3</sub> + ClO <sub>2</sub>	1026.86	1026.3	1026.0	1024
	str. OC'	690.84	693.0	695.7	691
	O'' <sub>2</sub> ClO umbrella	620.23	625.2	624.0	629.0
	as. bend. Cl'OO'' <sub>3</sub>	575.35	585.5	585.9	579.0
	as. bend. Cl'OO'' <sub>3</sub>	563.69			
	bend. ClO'' <sub>2</sub>	540.40	543.6	542.5	544
	s. bend. ClO'' <sub>2</sub> + str. ClO	479.59	486.6	486.6	
	bend. Cl'O'' <sub>2</sub> O + str. ClO	417.93 <sup>b</sup>			
	bend. Cl'O'' <sub>2</sub> O + ClO <sub>2</sub>	368.30	374.6	371.2	
	bend. Cl'OCi	243.49 <sup>b</sup>		238.0	
	O'' <sub>2</sub> Cl translation	214.91			
		110.82 <sup>b</sup>			
		53.69 <sup>b</sup>			
		34.97 <sup>b</sup>			

<sup>a</sup> In text; supplementary vibrational and spectral analysis were made with an AMPAC 5.0 package.<sup>111</sup> <sup>b</sup> Very weak.

**TABLE 4: Optimized Structure and Vibrational Frequencies ( $\text{cm}^{-1}$ ) of ClO<sub>3</sub>F**

	B3LYP	expt [112]
R(Cl–F) (Å)	1.647	1.619
R(Cl–O) (Å)	1.409	1.404
∠FCiO (°)	115.7	116.6
$\omega_4$ ( <i>e</i> )	1309.0	1315.6
$\omega_1$ ( <i>a<sub>1</sub></i> )	1059.8	1062.3
$\omega_2$ ( <i>a<sub>1</sub></i> )	691.7	712.4
$\omega_5$ ( <i>e</i> )	577.1	588.3
$\omega_3$ ( <i>a<sub>1</sub></i> )	528.4	547.5
$\omega_6$ ( <i>e</i> )	387.9	405.9

calculated in the spin-unrestricted approximation for the *T<sub>d</sub>*, *C<sub>3v</sub>*, and *C<sub>2v</sub>* structures. The numerical values are compared in Table 5 to the experimental data provided in the article of Grothe and Willner.<sup>12</sup> The *C<sub>3v</sub>* and *T<sub>d</sub>* structures present inconsistent values when compared to experimental data, whereas the correlation between experimental and calculated frequencies and intensities is rather good for the *C<sub>2v</sub>* structure.



**TABLE 5: Calculated Frequencies [ $\omega$  ( $\text{cm}^{-1}$ )], Intensities [ $I$  ( $\text{km}/\text{mole}$ )], and assignment in the  $T_d$ ,  $C_{3v}$ , and  $C_{2v}$  Space Groups of the  $\text{Cl}^{16}\text{O}_4$  and  $\text{Cl}^{18}\text{O}_4$  Isotopic Species vs Experiment<sup>12</sup>**

$T_d$			$C_{3v}$			$C_{2v}$			expt		
$\nu$	$I$	$\Gamma$	$\nu$	$I$	$\Gamma$	$\nu$	$I$	$\Gamma$	$\nu$	$I$	$\Gamma$
$\text{Cl}^{16}\text{O}_4$											
956.9	26.3	$A_1$	1198.1	181.5	$E$	1256.7	181.5	$B_2$	1234	s	$E$
937.6	5.5	$A_2$	992.3	1.3	$A_2$	1160.2	149.8	$A_1$	1161	vs	$A_1$
830.0	10.8	$E$	921.6	41.9	$A_1$	903.6	18.1	$A_1$	874	w	$A_1$
740.7	33.2	$F_1$	618.6	14.2	$E$	647.7	21.8	$B_1$	646	m	$E$
568.7	19.6	$F_2$	559.0	19.9	$A_1$	572.3	27.0	$A_1$	578	m	$A_1$
			504.7	2.7	$E$	549.7	14.8				
						412.5	2.0	$B_1$			
						85.4	1.7	$A_1$			
						375.3	0.0	$A_2$			
$\text{Cl}^{18}\text{O}_4$											
917.1	26.3	$A_1$	1158.3	26.3	$E$	1215.4	174.1	$B_2$	1196	s	$E$
883.7	1.6	$A_2$	937.6	1.6	$A_1$	1116.5	148.6	$A_1$	1118	vs	$A_1$
788.3	9.9	$E$	870.3	40.3	$A_1$	855.1	14.7	$A_1$	832	w	$A_1$
698.5	28.8	$F_1$	586.3	13.1	$E$	611.3	19.6	$B_1$	609	m	$E$
542.7	17.2	$F_2$	534.3	16.8	$A_1$	545.7	23.2	$A_1$	548	m	$A_1$
			478.3	2.1	$E$	525.1	12.7				
						403.8	1.8	$B_1$			
						364.1	1.4	$A_1$			
						353.8	0.0	$A_2$			

In spite this agreement, there is a slight discrepancy between the assignment of the IR spectra provided by the calculation and the experimental data which led Grothe and Willner<sup>12</sup> to postulate a  $C_{3v}$  symmetry for this radical. This assignment is supported by symmetry group arguments, namely six IR active modes for  $C_{3v}$  and eight for  $C_{2v}$  however, our calculations indicate that the low-frequency modes should have intensities close to zero and therefore another assignment, such as that reported here, is also consistent. However, we must note the inversion of the calculated  $\nu_1(B_2)$  and  $\nu_2(A_1)$  intensities with respect to the indications provided by Grothe and Willner.<sup>12</sup> These indications seem to refer to the peak heights, as displayed by Figure 1 of ref 12, rather than to integrated densities (band area). Though the height of  $\nu_1$  is about twice that of  $\nu_2$ , their band half widths are in the opposite ratio. Moreover, the interactions between the solute and the matrix may modify the intensities with respect to the gas phase. To confirm an assignment we have also performed structure and frequency calculations for the  $\text{FCIO}_3$  molecule, which clearly belongs to the  $C_{3v}$  point group and which is used by Grothe and Willner<sup>12</sup> as a reference system to assign the IR bands. Again, the theoretical results achieve a very good agreement with experiment. The zero-point energy calculated is of the order of magnitude of the potential energy barrier between the equivalent  $C_{2v}$  structures allowing inter-conversion between them. Two channels are possible. The first involves the symmetrical stretching mode  $\nu_3(A_1)$  and goes through the  $T_d$  saddle point, whereas the asymmetric stretching mode  $\nu_1(B_2)$  is responsible for the second route which involves the  $C_{3v}$  structure. The present theoretical results are in very good agreement with the recent calculations of Janoschek<sup>50</sup> and Van Huis and Schaefer III.<sup>21</sup> It is worth noting that except for the low-frequency modes below  $450 \text{ cm}^{-1}$ , the spin-restricted and spin-unrestricted schemes yield very close values for both  $\text{ClO}_3$  ( $C_{3v}$ ) and  $\text{ClO}_4$  ( $C_{2v}$ ).

**3.2. Monochlorine Oxide Anions  $\text{ClO}_x^-$ .** The ability of density functional methods to accurately describe negative ions has been numerically established by Galbraith and Schaefer.<sup>56</sup> The electron affinities are usually overestimated by at least 0.1 eV.<sup>57</sup> The hybrid HF/DFT methods appear to be particularly suitable as they provide reliable results on dipole bound anions

such as  $(\text{H}_2\text{O})_2^-$ .<sup>58</sup> All the mono-chlorine oxides are noticeably stabilized by the attachment of one electron. The adiabatic electron affinities of  $\text{ClO}$ ,  $\text{ClO}_2$ ,  $\text{ClO}_3$ , and  $\text{ClO}_4$  are calculated to be 2.23, 2.14, 4.07, and 5.1 eV, respectively. The  $\text{ClO}$  value is in very good agreement with the thermochemical determination of O'Hare and Wahl<sup>59</sup> ( $2.2 \pm 0.4$  eV) and with the estimate of Lee et al.<sup>60</sup> (2.17 eV). The value calculated for  $\text{ClO}_4$  is very large compared to the data reported in the *Handbook of Chemistry and Physics*;<sup>61</sup> however, it is within the range (4.7–6.0 eV) of the values calculated by different quantum chemical techniques.<sup>21</sup>

The relaxed geometries of the anions present a consistent lengthening of the  $\text{ClO}$  distances with respect to the corresponding neutral species. These distances are, respectively, 1.691, 1.571, and 1.495 Å for  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$ . For the  $\text{ClO}_4^-$  anion which belongs to the  $T_d$  point group the  $\text{Cl}-\text{O}$  distance is 1.451 Å, a value larger than the average of the  $\text{ClO}$  distances optimized in the  $C_{2v}$   $\text{ClO}_4$  radical. The  $\text{ClO}$  bond lengthening decreases as the chlorine coordination increases (i.e., 0.115, 0.092, 0.042, and 0.006 Å for  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$ , respectively). This can be interpreted as a consequence of the delocalization of the negative charge on an increasing number of centers. The  $\angle \text{OCIO}$  of  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  ( $113.9^\circ$  and  $108.1^\circ$ ) are smaller than those of the corresponding radicals, a tentative interpretation will be given in a next section.

**3.3. Di-Chlorine Oxides  $\text{Cl}_2\text{O}_x$ .** There are two possible isomers for the  $\text{Cl}_2\text{O}$  stoichiometry: the  $C_{2v}$   $\text{ClOCl}$  and the  $C_s$   $\text{ClClO}$ . The most stable is the  $C_{2v}$  isomer as evidenced by microwave<sup>62–64</sup> and electron diffraction<sup>65,66</sup> spectroscopies. The energy difference between the two isomers is calculated to be 12.29 kcal/mol. The present results coincide with those reported by Chaquin et al.,<sup>67</sup> who investigated several density functionals and by Lee, who performed CCSD(T) calculations.<sup>68</sup> The possible isomers of  $\text{Cl}_2\text{O}_2$  stoichiometry have been previously studied by different authors.<sup>51,53,69,70</sup> All these works conclude that the di-chlorine peroxide is the most stable isomer. Therefore, only  $\text{ClOOC}$  has been considered in the present study. As expected from the optimized structures of  $\text{ClO}$  and  $\text{ClOO}$ , the  $\text{ClO}$  bond is found 0.04 Å larger than the experimental one<sup>43</sup> whereas the  $\text{ClCl}$  bond length is too short by 0.06 Å. It is then consistent to expect an overestimation of the  $\text{OO}$  stretching frequency and an underestimation of the  $\text{ClO}$  ones. With respect to experiment<sup>71</sup> the  $\text{OO}$  stretching mode frequency is too large by  $90 \text{ cm}^{-1}$  whereas the  $\text{ClO}$  ones are in very good agreement. These discrepancies are not specific of the B3LYP approach since similar differences with respect to experiment are produced by other techniques such as MP/2 and CCSD(T)<sup>53</sup> and other density functionals.<sup>51</sup>

The  $\text{Cl}_2\text{O}_3$  system has been theoretically studied by Clark and Francisco,<sup>22</sup> who concluded that  $\text{ClOClOO}$  is the stable isomer. The agreement with the experimental data<sup>72,73</sup> is an indication of the overall quality of the approximate wave function.

Little or none is known of the structure and properties of the di-chlorine oxides  $\text{Cl}_2\text{O}_4$ ,  $\text{Cl}_2\text{O}_5$ ,  $\text{Cl}_2\text{O}_7$ , and  $\text{Cl}_2\text{O}_8$ , whereas  $\text{Cl}_2\text{O}_6$  has been known since 1843<sup>9</sup> and has been the subject of spectroscopic investigations in the solid state<sup>47</sup> and isolated in matrix.<sup>74</sup> The equilibrium geometry of the stablest isomer/conformer of each stoichiometry has been optimized, and the frequencies and intensities of its vibrational modes have been calculated. The stable isomer of  $\text{Cl}_2\text{O}_4$  is predicted to have an oxo structure  $\text{ClOClO}_3$  in which the  $\text{O}-\text{ClO}_3$  bond length is 1.74 Å and the  $\text{Cl}-\text{O}$  value, 1.686 Å, is close to the  $\text{ClO}$  radical value. Its calculated infrared spectrum is characterized by four

strong bands around 1285, 1270, 1037, and 630  $\text{cm}^{-1}$ , all other modes give rise to weak intensities. The head-to-tail dimer of  $\text{ClO}_2$  is observed in the crystalline phase of chlorine dioxide.<sup>75,76</sup> It is a diamagnetic complex which has been theoretically investigated by Harcourt<sup>17</sup> who explained the large intradimer ClO bond length by valence-bond arguments. For this structure, the B3LYP calculation finds a local minimum with a rather short intradimer ClO distance, i.e., 1.454 Å instead of 1.708 Å experimentally. In spite of the underestimation of the intermolecular distance, the dimer is calculated to be unstable with respect to the monomeric species at infinite separation. Therefore, the crystal should be stabilized by the dispersion forces which are neglected at the present level of calculation and by the long-range electrostatic interactions.

$\text{Cl}_2\text{O}_5$  is found to be a peroxide; in this case the Cl–O distance, 1.744 Å, is larger than in ClO and the O–ClO<sub>3</sub> distance, 1.812 Å, larger than in the oxo compound  $\text{Cl}_2\text{O}_4$ . Its calculated vibrational spectrum is very similar to that of  $\text{Cl}_2\text{O}_4$ , except the appearance of two medium bands around 890 and 650  $\text{cm}^{-1}$ . The structural, spectroscopic, and chemical properties of di-chlorine hexaoxide,  $\text{Cl}_2\text{O}_6$ , are present in many controversies.<sup>77,79</sup> Five possible structures have been proposed for this compound. The crystal structure has been determined by Tobias and Jansen,<sup>47</sup> it consists of an arrangement of ClO<sub>2</sub> and ClO<sub>4</sub> subunits which is consistent with the  $\text{O}_2\text{Cl–O–ClO}_3$  structure for the isolated molecule. Moreover, the analysis of the gas phase and matrix IR spectra enabled Jansen et al.<sup>74</sup> to conclude that only the  $\text{O}_2\text{Cl–O–ClO}_3$  structure is compatible with the observed spectral features. We have first investigated all possible structures with the 6-31G(d) basis set. Only two isomers happen to correspond to local minima of the energy surface:  $\text{O}_2\text{Cl–O–ClO}_3$  and the  $D_{3h}$   $\text{O}_3\text{Cl–ClO}_3$  ones. This latter is 23 kcal/mol higher in energy and has not been considered in the following discussion. For the  $\text{O}_2\text{Cl–O–ClO}_3$  system all the calculated and observed frequencies are in a surprising satisfactory agreement. With respect to the crystal structure, there are some severe discrepancies in the ClO bond length which are due to the almost ionic structure of the crystal—i.e.,  $\text{ClO}_2^+$ ,  $\text{ClO}_4^-$ —as reflected by the tetrahedralization of the ClO<sub>4</sub> group and by the CsCl arrangement of the ions. Moreover, the infrared spectrum recorded in the crystal phase<sup>47</sup> is rather different than the matrix isolation one, and therefore this solid can hardly be considered as a molecular crystal. The quantum chemically optimized structure should be closer to the real isolated molecule than that given for the crystal phase. The striking features of this structure is on the one hand the value of the  $\text{O}_2\text{Cl–O}$  distance, 1.955 Å, which is similar to that optimized for  $\text{Cl}_2\text{O}_3$ , the other system containing a ClO<sub>2</sub> termination. On the other hand, the O–ClO<sub>3</sub> distance is shorter by more than 0.1 Å than the corresponding bond length in  $\text{Cl}_2\text{O}_4$  and  $\text{Cl}_2\text{O}_5$ .  $\text{Cl}_2\text{O}_7$  is predicted to be an oxo di-chlorine oxide with an almost  $C_s$  symmetry. The distance between the ClO<sub>3</sub> groups and the bridging oxygen is 1.74 Å as in  $\text{Cl}_2\text{O}_4$ . In the peroxy structure of  $\text{Cl}_2\text{O}_8$  this latter bond length is larger than that optimized in  $\text{Cl}_2\text{O}_8$  whereas the O–O bond is slightly shorter. Note that the stable isomer has a gauche conformation such as  $\text{Cl}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$ . The calculated infrared spectra are quite different.  $\text{Cl}_2\text{O}_7$  is characterized by a strong doublet at about 1300  $\text{cm}^{-1}$  and a strong band at 480  $\text{cm}^{-1}$ , whereas the  $\text{Cl}_2\text{O}_8$  spectrum has a unique strong band at 1276  $\text{cm}^{-1}$  and four medium ones at 1263, 1252, 1009, and 600  $\text{cm}^{-1}$ .

**3.4. Energetics.** The total energies of the different compounds are given in Table 1 while important information can be obtained from the relative trends in the corresponding dimerization and

**TABLE 6: Dimerization and Dissociation Energies (kcal/mol)**

$\text{Cl}_2\text{O}_x$ compound $\rightarrow$ products	calcd	expt
$\text{Cl}_2\text{O}_2 \rightarrow 2\text{ClO}$	14.68	17 [51]; 13.5 [13]
$\text{Cl}_2\text{O}_3 \rightarrow \text{ClO} + \text{OCIO}$	8.59	11.1–14.8 [22]
$\text{Cl}_2\text{O}_4 \rightarrow \text{ClO} + \text{ClO}_3$	19.88	35.2 [13]
$\text{Cl}_2\text{O}_5 \rightarrow \text{ClOO} + \text{ClO}_3$	4.82	20 [13]
$\text{Cl}_2\text{O}_5 \rightarrow \text{ClO} + \text{ClO}_4$	23.46	23.7 [13]
$\text{Cl}_2\text{O}_6 \rightarrow 2\text{ClO}_3$	24.21	43.9 [13]
$\text{Cl}_2\text{O}_6 \rightarrow \text{OCIO} + \text{ClO}_4$	16.87	20.9 [13]
$\text{Cl}_2\text{O}_7 \rightarrow \text{ClO}_3 + \text{ClO}_4$	25.32	33.0 [13]
$\text{Cl}_2\text{O}_8 \rightarrow 2\text{ClO}_4$	32.62	31.7 [13]

dissociation channels which are listed in Table 6. All these dissociation channels correspond to endothermic processes. The results point out that the stability order and therefore the dissociation energies are very dependent on the corresponding dissociation channels. The reactive channels corresponding with the cleavage of the peroxy bonds,  $-\text{O}-\text{O}-$  ( $\text{Cl}_2\text{O}_2$ ,  $\text{Cl}_2\text{O}_5$ , and  $\text{Cl}_2\text{O}_8$ ) and yielding chlorine trioxide (ClO<sub>3</sub>) and chlorine tetraoxide (ClO<sub>4</sub>) as dissociation products present the larger values of the dimerization or dissociation energies. Thus, it should be reasonable to conclude that systems with this bond type are rather stable while ClO<sub>3</sub> and ClO<sub>4</sub> tend to form complexes and dimers.

#### 4. Bonding in the Monochlorine and Di-Chlorine Oxides Series

The bonding in the mono-chlorine and di-chlorine oxides series has not been investigated so far in a systematical way though it raises several problems and may explain the high reactivity of these compounds. For instance, it should be interesting to locate the regions of excess spin density of the mono-chlorine oxides which have an odd number of electrons. Moreover, the chlorine–oxygen bond is not well understood, many models such as those discussed in refs 17 and 21 rely on the three-electron picture introduced by Pauling<sup>24</sup> in order to explain the bonding in ClO<sub>2</sub>. Another aspect is the actual valence of the chlorine atom which formally varies from one to four provided the Cl–O bonds are mostly dative. The discussion presented hereafter is based on the topological analysis sketched in the next paragraph.

**4.1. A Sketch of the Topological Analysis of the ELF Function.** The concepts of chemical bond and of chemical structure belong to an intuitive system of representation of the matter settled by the chemists on the basis of experience. They are not physical observables in the sense of the quantum mechanics. The quantum mechanics is the physical theory which fully accounts for the stability and for the properties of molecules and solids. It provides a non local description in terms of expectation values of operators. However, the ideas underlying the qualitative theories of the chemical structure intend to provide a local representation in terms of bonds between atoms and of electron lone pairs.<sup>80</sup> The link with quantum mechanics is made by several quantum chemical methods such as molecular orbital localization<sup>81–83</sup> and projection-based population analysis.<sup>84–90</sup> The weakness of these methods is that they contain some arbitrariness (i.e., the choice of the localization criterion, of the expansion basis) and that their applicability is limited to given classes of approximate computational schemes (for example, the Mulliken population analysis is only conceivable

in the LCAO framework). Alternatively, topological methods<sup>91–93</sup> enable a partition of the molecular space into regions having a chemical signification without transgressing the postulates of quantum mechanics. The topological analysis of the electron localization function of Becke and Edgecombe<sup>93,94</sup> is particularly well-adapted to the discussion of the nature of chemical bonds.

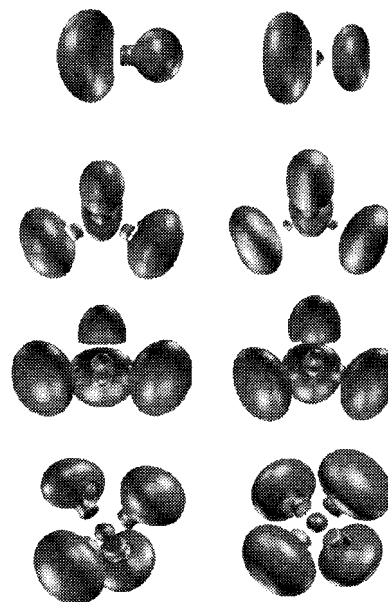
The electron localization function (ELF) introduced by Becke and Edgecombe<sup>94</sup> is a local function which describes how much the Pauli repulsion is efficient at a given point of the molecular space. In the seminal paper of Becke and Edgecombe, ELF was derived from the Laplacian of the conditional probability  $\nabla^2 P_{\text{cond}}(\mathbf{r}_1, \mathbf{r}_2)_{\mathbf{r}_1=\mathbf{r}_2}$ . An alternative interpretation has been given by Savin et al.<sup>95</sup> in terms of the local excess kinetic energy density due to Pauli principle. This interpretation not only gives deeper physical meaning to the ELF function but also allows us to generalize ELF to any wavefunction and in particular to the exact one. Therefore ELF provides a rigorous basis for the analysis of the wavefunction and of the bonding in molecules and crystals. In 1994, it was proposed to use the gradient field of ELF in order to perform a topological analysis of the molecular space<sup>93</sup> in the spirit of Bader's theory of atoms in molecules.<sup>91</sup> The attractors of ELF determine basins which are either core basins, labeled by  $C(X)$ , encompassing nuclei or valence basin when no nucleus except a proton lies within it. The valence basins,  $V(X_1, X_2, \dots)$ , are characterized by the number of core basins with which they share a common boundary, this number is called the valence basin synaptic order.<sup>96</sup> There are therefore asynaptic, monosynaptic, disynaptic, and polysynaptic valence basins. Monosynaptic basins usually correspond to lone-pair regions whereas di- and polysynaptic basins characterize chemical bonds. An advantage of this representation is that it provides a clear criterion to identify multicentric bonds. In a way, this is a complementary view to the traditional valence representation: instead of counting bonds from a given center which only accounts for two body links, the count is performed from the "piece of glue" which sticks the atoms together. In this approach the attractor basins are transformed by symmetry operations according to the totally symmetric representation of the molecule point group. In general, attractors are single points except for systems belonging to a continuous group. For atoms, off-center attractors are therefore spherical whereas off-axis attractors of linear molecules are circles. Graphical representations of the bonding are obtained by plotting isosurfaces of the localization function which delimit volumes within which the Pauli repulsion is rather weak. These latter, the localization domains, are called irreducible when they contain one and only one attractor.

This method also provides a tool for the study of the evolution of the bonding along a reaction pathway. In the topological context, the transformation of the bonding finds expression in the appearance and disappearance of local maxima which can be studied with the help of Thom's Catastrophe Theory.<sup>97</sup> The Catastrophe Theory has been first applied to the analysis of the electron charge density of reacting systems<sup>98–101</sup> and more recently extended to the ELF function.<sup>102</sup> This latter approach provides a clear distinction between covalent and dative bond which is consistent with Lewis definitions.

From a quantitative point of view a localization basin (core or valence) is characterized by its population, i.e., the integrated one-electron density over the basin:

$$\bar{N}(\Omega_i) = \int_{\Omega_i} \rho(\mathbf{r}) \, d\mathbf{r} \quad (1)$$

in which  $\rho(\mathbf{r})$  denotes the one electron density at  $\mathbf{r}$  and  $\Omega_i$  is



**Figure 4.** Localization domains of the  $\text{ClO}_x$  (left) and  $\text{ClO}_x^-$  (right) systems. This figure, presented here in black and white, is available in color as Supporting Information.

the volume of the basin. In the case of open-shell systems, the basin integrated spin density is defined as

$$\langle S_z \rangle_{\Omega_i} = \frac{1}{2} \int_{\Omega_i} (\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})) \, d\mathbf{r} \quad (2)$$

It is also worthy to calculate the variance of the basin population:

$$\sigma^2(\bar{N}; \Omega_i) = \int_{\Omega_i} d\mathbf{r}_1 \int_{\Omega_i} \pi(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 - [\bar{N}(\Omega_i)]^2 \quad (3)$$

where  $\pi(\mathbf{r}_1, \mathbf{r}_2)$  is the spinless pair function.<sup>103</sup> Its square root, the standard deviation, represents the quantum mechanical uncertainty on  $\bar{N}(\Omega_i)$ . It has been shown that the variance can be readily written as a sum of contributions arising from the other basins:<sup>104</sup>

$$\sigma^2(\bar{N}; \Omega_i) = \sum_{j \neq i} \bar{N}(\Omega_i) \bar{N}(\Omega_j) - \bar{N}(\Omega_i, \Omega_j) \quad (4)$$

In this expression  $\bar{N}(\Omega_i) \bar{N}(\Omega_j)$  is the number of electron pairs classically expected from the basin population whereas  $\bar{N}(\Omega_i, \Omega_j)$  is the actual number of pairs obtained by integration of the pair function over the basins  $\Omega_i$  and  $\Omega_j$ . It is worthy noting that this expression of the basin population variance provides a natural picture of the electron delocalization. Another interesting feature of the population analysis outlined above is that it allows us to propose valence bond resonance structures on a firm basis.

**4.2. Mono-Chlorine Oxides and Peroxides.** Figure 4 displays the localization domains of the  $\text{ClO}_x$  oxides and of their anion. For all the systems the Cl–O bonds are characterized by a disynaptic basins  $V(\text{Cl}, \text{O})$ . The monosynaptic basins  $V(\text{Cl})$  and  $V(\text{O})$  in  $\text{ClO}$  and  $\text{ClO}^-$  have circular attractors according to the  $C_{\infty v}$  symmetry of these systems. For the other systems the monosynaptic basins of the oxygen atoms are not well-separated because the local symmetry of the electron–nucleus potential is almost axial. In the  $\text{ClO}_2$  molecule there are two monosynaptic basins  $V(\text{Cl})$  symmetrically located on each side of the molecular plane.

Table 7 reports the topological population analysis of the mono-chlorine oxides. The monosynaptic basins of each given center have been merged in order to simplify the discussion.



TABLE 7: ClO<sub>x</sub> and ClO<sub>x</sub><sup>-</sup> Molecules<sup>a</sup>

basin	Cl-O	$\bar{N}(\Omega_i)$	$\sigma(\bar{N}(\Omega_i))$	$S_z(\Omega_i)$
ClO				
C(Cl)		10.1	0.75	0.01
C(O)		2.1	0.58	0.02
V(Cl)		6.0	1.11	0.14
V(O)		5.6	1.06	0.31
V(Cl, O)	1.576	1.1	0.90	0.01
ClO <sup>-</sup>				
C(Cl)		10.1	0.75	
C(O)		2.1	0.60	
V(Cl)		6.5	1.03	
V(O)		6.6	1.11	
V(Cl, O)	1.691	0.6	0.71	
ClO <sub>2</sub>				
C(Cl)		10.1	0.75	0.01
C(O)		2.1	0.58	0.01
V(Cl)		4.3	1.27	0.17
V(O)		5.9	1.17	0.15
V(Cl, O)	1.479	1.25	0.94	0.0
ClO <sub>2</sub> <sup>-</sup>				
C(Cl)		10.1	0.75	
C(O)		2.1	0.58	
V(Cl)		5.0	1.27	
V(O)		6.4	1.32	
V(Cl, O)	1.576	1.0	0.84	
ClO <sub>3</sub>				
C(Cl)		10.1	0.76	0.01
C(O)		2.1	0.58	0.01
V(Cl)		2.2	1.07	0.14
V(O)		6.0	1.27	0.10
V(Cl, O)	1.453	1.4	0.90	0.01
ClO <sub>3</sub> <sup>-</sup>				
C(Cl)		10.1	0.75	
C(O)		2.1	0.58	
V(Cl)		2.6	1.06	
V(O)		6.3	1.14	
V(Cl, O)	1.495	1.4	0.96	
ClO <sub>4</sub>				
C(Cl)		10.1	0.76	0.01
C(O)	1.488	2.2	0.60	0.0
C(O)	1.414	2.2	0.60	0.02
V(O)	1.488	5.7	1.137	0.22
V(O)	1.414	5.9	1.17	0.0
V(Cl, O)	1.488	1.6	1.03	0.0
V(Cl, O)	1.414	2.0	1.10	0.0
ClO <sub>4</sub> <sup>-</sup>				
C(Cl)		10.1	0.75	
C(O)		2.1	0.58	
V(O)		6.3	1.14	
V(Cl, O)	1.457	1.8	0.96	

<sup>a</sup> ClO bond optimized bond length (Å), basin populations  $\bar{N}(\Omega_i)$ , standard deviation  $\sigma(\bar{N}(\Omega_i))$ , and integrated spin densities  $S_z(\Omega_i)$ .

In the molecular orbital approach, the electronic structure of ClO in the ground state is described by the single determinantal wave function:

$$\psi = \dots [7\sigma]^2 [2\pi]^4 [3\pi]^3 \quad (5)$$

in which the  $7\sigma$  and  $2\pi$  are bonding molecular orbitals whereas  $3\pi$  is anti-bonding. The expected bond order is therefore  $3/2$ . This picture is consistent with that proposed by Pauling<sup>24</sup> for FO in terms of a single bond and of a three-electron bond, i.e.,  $\text{:}\ddot{\text{F}} \text{---} \ddot{\text{O}}\text{:}$ , because this latter three-electron bond is counted for half a single bond the resulting bond order is also  $3/2$ . In the case of benzene, the bond order of the C-C bonds are also  $3/2$  and the related basin population  $V(\text{C}, \text{C})$  calculated within the topological analysis of ELF is 2.8,<sup>96</sup> a value in agreement with

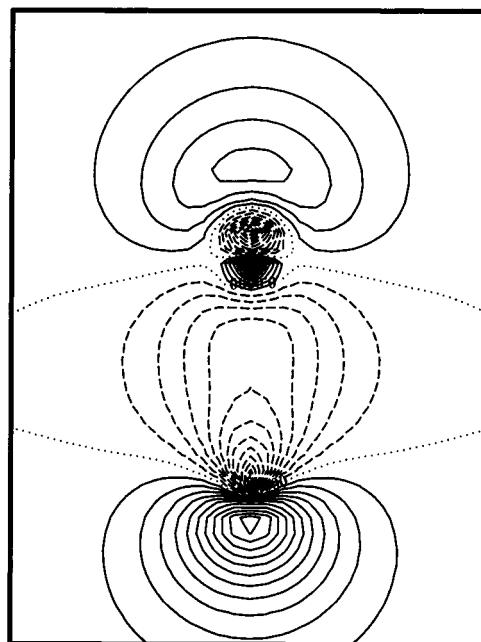


Figure 5. Plot of the  $7\sigma$  molecular orbital in a plane containing the internuclear axis. The isoline separation is 0.05. Full, dotted, and dashed lines correspond to positive, zero, and negative values.

the topological bond orders derived by Cioslowski and Mixon<sup>105</sup> and by Ángyán et al.<sup>106</sup> in the framework of the theory of atoms in molecules. On this basis one can expect a rather large population of the V(Cl, O) basin. In fact the calculation yields  $1.1 e^-$ , in agreement with the AIM bond order 0.41. This result can be explained by considering the  $7\sigma$  orbital displayed in Figure 5. In this figure the dotted lines materialize the intersections of the nodal surface with the reference plane, in agreement with the interpretation of ELF given by Burdett<sup>107</sup> these nodal surfaces are close to the separatrices of the V(Cl, O) basin and therefore  $7\sigma$  noticeably contributes to the electron density in the lone-pair regions. The analysis of the V(Cl, O) population in terms of orbital contributions indicates that  $0.5 e^-$  is provided by  $7\sigma$ , the remaining integrated density being brought by the two degenerate  $2\pi$ , moreover  $7\sigma$  brings 0.4 and  $1.0 e^-$  to V(Cl) and V(O), respectively.

Within the ClO<sub>x</sub> series the V(Cl, O) basin population increases with the chlorine coordination, a result which is consistent with the evolution of the ClO bond lengths. As a general rule, the standard deviation of this population is always rather large, indicating an electron delocalization involving the oxygen and chlorine monosynaptic basins. Except for the shortest ClO bonds of ClO<sub>4</sub>, the V(Cl, O) basin populations are less than 2.0 the value expected for a single bond. The integrated spin densities show that the odd electron is located in the V(O) and V(Cl) basins in ClO, ClO<sub>2</sub>, and ClO<sub>3</sub> and only on the oxygen involved in the largest ClO bonds in ClO<sub>4</sub>, in agreement with the antibonding character of the singly occupied molecular orbital. It is worth noting that  $S_z(\text{V}(\text{Cl}, \text{O}))$  is always negligible. Following Pauling's description of ClO<sub>2</sub> in terms of three-electron bonds,<sup>24</sup> several authors<sup>17,21</sup> have invoked similar resonance structures to describe the ClO bonds. Our analysis finds that the weight of such structures should be very small because the odd electron is almost not located on the ClO bond; moreover, the small V(Cl, O) populations indicate that ionic and neutral nonbonded structures have to be considered.

The populations of monosynaptic basins V(O) and V(Cl) in the anionic species are always larger than the corresponding ones in the neutral species. Except for the ClO<sub>4</sub>/ClO<sub>4</sub><sup>-</sup> pair, the



V(Cl, O) population follows the opposite trend. These two results are in agreement with the lengthening of the ClO bond observed in the geometry optimization process and so which seems to be due to the increase of the repulsive forces between the chlorine and oxygen centers. In the case of ClO<sub>4</sub> the symmetry is increased from C<sub>2v</sub> to T<sub>d</sub>, in the anion the Cl–O distances as well as the V(Cl, O) populations are close to the averages of the corresponding values in the radical, but nonetheless larger. The increase of the chlorine monosynaptic basin populations in ClO<sub>2</sub><sup>−</sup> and ClO<sub>3</sub><sup>−</sup> with respect to the neutral species enhances the relative contribution of the chlorine lone pair–oxygen repulsion to the molecular potential and therefore yields a narrowing of the ∠ OClO bond angles.

In all mono-chlorine oxides, the total populations of the monosynaptic basins V(O) are close to 6 e<sup>−</sup> which corresponds to the number of valence electrons of the oxygen atom, therefore the ClO bonds are expected to be dative bonds. The dissociation reaction can be written as:



According to the stoichiometry, the electron donor product, ClO<sub>x−1</sub>, belongs either to a continuous symmetry group (x ≤ 2) or to a finite one otherwise. In the former case, the stretching of a Cl–O bond induces an electronic transfer from the V(Cl, O) toward the V(Cl) basin. At an internuclear separation near 2.25 Å, V(Cl, O) vanishes. For x ≥ 3, the V(Cl, O) disynaptic basin of the stretched bond becomes monosynaptic as a critical bond length is reached. The population of this basin increases as the bond length is increased due to an electronic transfer from the remaining V(Cl, O) basins. From the topological point of view<sup>102</sup> the breaking of a dative bond can be achieved either by a miomorphic process in which the number of basins decreases or by an isomorphic diffeosynaptic one in which the number of basins remains constant but at least the synaptic order of one basin changes. The former mechanism occurs when the electron donor product belongs to a continuous symmetric group, the latter otherwise.

**4.3. Mono-Chlorine Peroxides.** The populations, population standard deviations, and integrated spin densities of the basin of the mono-chlorine peroxides are reported in Table 8 together with those of the dioxygen molecule in its ground state. In ClOO, there is no disynaptic basin linking oxygen to chlorine, the weak ClO bond can be explained by a small charge transfer of an amount of about 0.1 e<sup>−</sup> from the dioxygen subunit toward the chlorine center. The analysis of the variance also indicates that a noticeable delocalization occurs. The V(O), V(Cl), V(O′), and V(O, O′) are involved in the delocalization since the respective contributions of the three latter basins to the variance of the V(O) population are, respectively, 27%, 33%, and 22%. The populations within the OO′ subunit are close to those calculated for the dioxygen molecule. Note, however, the weakening of the OO′ bond with respect to O<sub>2</sub> and the polarization which transfers 0.1 e<sup>−</sup> from the bridging oxygen to the terminal one. The integrated spin density localizes the odd electron on the oxygen monosynaptic basins, in other words on the lone pairs. The picture provided by the ELF analysis is that of a dioxygen molecule in interaction with a chlorine atom.

In the same way, ClOOO can be described in terms of an interaction between ClO and O<sub>2</sub>. There is no disynaptic basin between the two moieties which have the same overall topologies as ClO and O<sub>2</sub>. The basin populations in the O′O′′ subsystem are identical to the corresponding ones in ClOO. In the ClO part, the bonding is weaker than in the free radical: on one hand the V(Cl, O) basin population is halved and on the

**TABLE 8: O<sub>2</sub>, ClOO, and ClOOO Molecules<sup>a</sup>**

basin	$\bar{N}(\Omega_i)$	$\sigma(\bar{N}(\Omega_i))$	$S_z(\Omega_i)$
O <sub>2</sub>			
C(O)	2.1	0.59	0.04
V(O)	5.2	1.13	0.46
V(O, O)	1.3	0.94	0.01
ClOO′			
C(Cl)	10.1	0.76	0.01
C(O)	2.1	0.58	0.01
C(O′)	2.1	0.58	0.02
V(Cl)	7.0	1.10	−0.0
V(O)	5.1	1.25	0.20
V(O′)	5.4	1.25	0.26
V(O, O′)	1.2	0.88	0.0
ClOO′O′′			
C(Cl)	10.1	0.74	0.0
C(O)	2.1	0.58	0.0
C(O′)	2.1	0.58	0.02
C(O′′)	2.1	0.58	0.02
V(Cl)	6.3	1.14	−0.04
V(O)	5.7	1.10	−0.12
V(O′)	5.1	1.11	0.29
V(O′′)	5.4	1.13	0.34
V(Cl, O)	1.0	0.90	0.0
V(O′, O′′)	1.2	0.98	0.0

<sup>a</sup> Basin populations  $\bar{N}(\Omega_i)$ , standard deviation  $\sigma(\bar{N}(\Omega_i))$ , and integrated spin densities  $S_z(\Omega_i)$ .

other hand both monosynaptic basins V(O) and V(Cl) populations are increased. These effects are consistent with a ClO distance larger in ClOOO than in ClO.

**4.4. Di-Chlorine Oxides and Peroxides.** In the series of di-chlorine oxides investigated in this paper, the only ClCl bond may be found in ClClO which appears to be a peculiar system with respect to the topology of the electron localization function. On one hand this molecule appears to be a ClO radical interacting with a chlorine atom in the same way as ClOO has been previously described in terms of Cl interacting with O<sub>2</sub>. The valence basin populations of the ClO subunit are close to those of the free radical, for example the V(Cl, O) population is 1.0 e<sup>−</sup>. However, this subunit is polarized since the total population of V(Cl) basins is lower in ClClO than in ClO by about 0.6 e<sup>−</sup> which are transferred to the oxygen V(O) basin. On the other hand, each chlorine possesses a small monosynaptic basin located on the Cl–Cl axis. This situation is very similar to that encountered in the covalent dissociation of the ethane molecule described in ref 102: at internuclear distances less than the critical distance  $d^*$  the bond is characterized by the attractor of the disynaptic basin, at  $d^*$  a cusp catastrophe occurs which splits the disynaptic basin into two monosynaptic ones. As there is not an energetical transition state for such reactions, the topology with two monosynaptic basins corresponds to a region of attractive interaction between the fragments. The internuclear distance of Cl<sub>2</sub> optimized at the 6-311+g(3df)/B3LYP level is 2.009 Å (1.988 Å experimentally<sup>108</sup>). At this separation the topology of the ELF function presents a disynaptic basin, the attractor of which is located at bond midpoint. The population of this basin is 0.7 e<sup>−</sup>. When the internuclear distance is increased there is an electronic transfer toward the chlorine lone pairs and at  $d^* \sim 2.1$  Å the disynaptic basin splits into two monosynaptic ones. It is then reasonable to imagine homolytic bonds involving electronegative atoms for which the energy minimum corresponds to this latter topology and we propose to call such bonds “protocovalent”.

The valence basin populations of the remaining di-chlorine oxides and peroxides are reported in Table 9. The populations of the V(O) and V(Cl, O) basins of the ClO<sub>2</sub> and ClO<sub>3</sub> groups

**TABLE 9: Valence Basin Populations of the Di-Chlorine Oxides<sup>a</sup>**

ClO <sub>x</sub> OClO <sub>x</sub> Compounds						
	V(Cl)	V(Cl')	V(O)	V(Cl, O)	V(Cl', O)	
ClOCl'	6.4	6.4	5.5	0.6	0.6	
ClOCl'O <sub>2</sub>	6.5	3.6	6.0	0.8		
ClOCl'O <sub>3</sub>	6.4		5.4	0.8	0.9	
ClO <sub>3</sub> OCl'O <sub>3</sub>	3.4		5.4		1.4	
Peroxides						
	V(Cl)	V(O)	V(O')	V(Cl, O)	V(O, O')	V(Cl', O')
ClOO'Cl'	6.6	5.4	5.4	0.6	0.7	0.6
ClOO'Cl'O <sub>3</sub>	6.5	5.3	5.7	0.7	0.7	1.1
ClO <sub>3</sub> OO'Cl'O <sub>3</sub>		5.7	5.7	1.2	0.8	1.2
ClO <sub>2</sub> groups						
	V(Cl, O)			V(O)		
Cl <sub>2</sub> O <sub>3</sub>	1.4			6.0		
Cl <sub>2</sub> O <sub>6</sub>	1.6			5.8		
ClO <sub>3</sub> groups						
	V(O)	V(O')	V(Cl, O)	V(Cl, O')		
Cl <sub>2</sub> O <sub>4</sub>	5.9	5.9	1.9	1.9		
Cl <sub>2</sub> O <sub>5</sub>	6.0	5.9	1.7	1.9		
Cl <sub>2</sub> O <sub>6</sub>	6.1	5.9	1.8	1.9		
Cl <sub>2</sub> O <sub>7</sub>	6.0	5.9	1.8	1.9		
Cl <sub>2</sub> O <sub>8</sub>	6.0	5.9	1.7	1.9		

<sup>a</sup> In the ClO<sub>2</sub> groups of Cl<sub>2</sub>O<sub>3</sub> and Cl<sub>2</sub>O<sub>6</sub> the two oxygens are almost equivalent. In the ClO<sub>3</sub> groups the plane defined by the bridging oxygen, the chlorine, and the oxygen labeled O<sub>I</sub> in Cl<sub>2</sub>O<sub>7</sub> on Figure 3 forms a pseudo symmetry element for the almost equivalent oxygens O<sub>II</sub> and O<sub>III</sub>. In the relevant part of the table, O<sub>I</sub> is denoted by O, and O<sub>II</sub> and O<sub>III</sub> by O'.

are very similar to the corresponding ones in ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, respectively. However, the chlorine V(Cl) populations are larger in Cl<sub>2</sub>O<sub>3</sub> and Cl<sub>2</sub>O<sub>6</sub> than in ClO<sub>3</sub><sup>-</sup>. The V(Cl) population of the terminal chlorides both oxides and peroxides is 6.5 ± 0.1e<sup>-</sup>. Considering now the interaction between a chlorine atom and a bridging oxygen, it must be first mentioned that for internuclear Cl–O distances larger than 1.9 Å there is no disynaptic basin. This situation occurs only in the systems involving a ClO<sub>2</sub> group, namely Cl<sub>2</sub>O<sub>3</sub> and Cl<sub>2</sub>O<sub>6</sub>. There are four kinds of ClO bonds which possess a disynaptic V(Cl, O) according to the chlorine coordination (1 or 4) and to the bridging oxygen type (oxo or peroxy). For each of them the V(Cl, O) population appears to be characteristic: ~0.65e<sup>-</sup> for Cl(1)O(peroxy), 0.8 e<sup>-</sup> for Cl(1)O(oxo), 0.9 e<sup>-</sup> for Cl(4)O(oxo), and ~1.15e<sup>-</sup> for Cl(4)O(peroxy). It is worth noting that the Cl(4)O(peroxy) populations are larger than the Cl(4)O(oxo) ones, though the ClO distances are in the opposite order. Finally, the V(O, O) populations in the peroxides are of the order of 0.75 e<sup>-</sup>.

The sum of the populations of the valence basin around a given center, the atomic valence population, enables us to check if the octet rule is satisfied. These sums are 6.85 ± 0.45e<sup>-</sup> and 7.4 ± 0.7e<sup>-</sup> around chlorine and oxygen, respectively. The topological analysis provides a picture different from the octet rule: around the most electropositive atom the atomic valence population is close to the number of valence electrons of the isolated atom, whereas for the most electronegative one it tends to satisfy the octet rule. Indeed, rather than the octet rule it is the “democracy principle” asserted by D. L. Cooper and co-workers<sup>109</sup> which governs the electronic distributions.

## 5. Conclusion

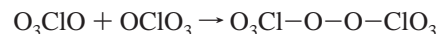
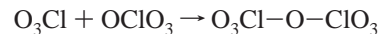
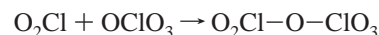
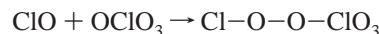
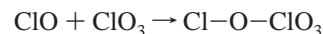
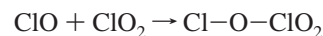
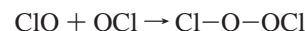
From the results presented in this paper it is possible to draw some general conclusions on the reactivity of the ClO<sub>x</sub> oxides. The most striking property of these compound is their large

electron affinities. The dissociation energies of the di-chlorine oxides and peroxides listed in Table 6 appear to be correlated to the affinities of the fragments. The main characteristic of the bonding in the mono-chlorine oxides is that the spin density is distributed on the chlorine and oxygen lone pairs and negligible on the bond. It is attractive to assume that the reactive center corresponds to the atom which has the largest integrated spin density over its monosynaptic basin. Accordingly, the reactive center is located on oxygen in ClO and ClO<sub>4</sub>, on chlorine in ClO<sub>2</sub> and ClO<sub>3</sub>. Moreover, the ClCl bonds are rather weak and correspond to mutual approaches in which the dipole moments of the neutral fragments are in opposite directions, which hampers the formation of the ClCl bonds in the complexation processes. This leads us to propose the three following rules for the complexation reactions:

(1) The chemical bond which links the two mono-chlorine fragments of a di-chlorine oxide or peroxide is formed between their reactive centers and determines the structure.

(2) The formation of a ClCl bond is not favored.

(3) The complexation energy is roughly proportional to the sum of the electron affinities. The structures of the stable isomers of the Cl<sub>2</sub>O<sub>x</sub> compound satisfy the requirements of the two first rules and cover all the allowed possibilities:



For all these reactions, the pathway is straightforward and it is reasonable to expect there are no transition states or very low barriers. From the reaction energies of Table 6 and from the electron affinities, the dimerization of ClO<sub>3</sub> appears to be thermodynamically favored with respect to the formation of Cl<sub>2</sub>O<sub>6</sub> from ClO<sub>2</sub> and ClO<sub>4</sub>. This reaction which is probably the necessary exception to these rules should involve a transition state. It should be interesting to explore the two reaction channels in the future.

**Supporting Information Available:** Table 3S and the color version of Figure 4 (color code: magenta = core, red = valence monosynaptic, green = valence disynaptic). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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