Molecular Structures and Electron Affinities for the Chlorine Oxides ClOO, ClOOO, and ClO_3 (C_{3v})

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The molecular structures and energetics of ClOO, ClOOO, and ClO_3 (C_{3v}) have been studied using four independent density functional theory methods. The methods used have been carefully calibrated against a comprehensive tabulation of experimental electron affinities (*Chem. Rev.* **2002**, *102*, 231). Optimized geometries, adiabatic electron affinities, vertical electron affinities, and vertical detachment energies are reported. Vibrational frequencies and bond dissociation energies are also reported. These density functional theory methods were utilized in conjunction with the double-ζ plus polarization basis set augmented with diffuse s-type and p-type functions (DZP++). Among these, the unrestricted BHLYP and B3LYP methods used for the open-shell ClOO and ClOOO systems lead to serious spin contamination, while the BLYP and BP86 methods have relatively little spin contamination ($\langle S^2 \rangle < 0.76$). The reliable predicted adiabatic electron affinities with the BLYP functional are 3.33 (ClOO), 3.97 (ClO_3), and 2.84 (ClOOO) eV. The electronic ground state of $ClOO^-$ is a triplet ($^3A''$) state. There are seven local minima on the potential energy surface for $ClOOO^-$; among them the gauche structure is the global minimum. The $ClOO^-$ and $ClOOO^-$ ground states may be regarded as $Cl^- \cdots O_2$ and $Cl^- \cdots O_3$ complexes, respectively. The $ClOO^-$ anion triplet state is predicted to lie 49−52 kcal/mol below $OClO^-$. The neutral ClOOO isomer is predicted to lie 57 kcal/mol below the C_{3v} structure ClO_3. *gauche*-$ClOOO^-$ is predicted to lie 31 kcal/mol (BLYP) below the ClO_3^- (C_{3v}) structure.

Introduction

Research on the chlorine photosensitized decomposition of ozone in the stratosphere has focused attention on the oxides and peroxides of chlorine.[1−5] The possible reaction mechanisms and properties of ClO_n have been extensively investigated by many research groups both experimentally and theoretically.[6−13] Some experimental structures and fundamental vibrational frequencies for the ClO_n series have been determined from infrared (IR) spectra with the matrix isolation technique,[14−21] but the existence and stability of ClOOO remain matters of some dispute. The importance of negative ions in atmospheric chemistry is well established.[22,23] The theoretical structures and electron affinities of ClO, ClO_2 (C_{2v}), and ClO_4 have been examined with density functional theory methods in our earlier work,[24,25] but we have not yet investigated the ClOO, ClOOO, and ClO_3 (C_{3v}) species.

Density functional theory (DFT) in conjunction with DZP++ basis sets has been shown to be successful in predicting the electron affinities (EAs) of many inorganic species, such as BrO_n/BrO_n^- and BrF_n/BrF_n^-.[26] These studies and others have demonstrated that the better DFT/DZP++ methods generally yield accurate EAs. The reliability of these schemes is also well established for the prediction of molecular structures.

The purpose of the present study is to systematically apply four modern DFT methods to the theoretical prediction of the electron affinities of ClOO, ClOOO, and ClO_3 (C_{3v}), as well as their equilibrium geometries, dissociation energies, and harmonic vibrational frequencies.

Of specific interest are three neutral−anion energy differences:
(a) the adiabatic electron affinity

$$EA_{ad} = E(\text{optimized neutral}) - E(\text{optimized anion})$$

(b) the vertical electron affinity

$$EA_{vert} = E(\text{optimized neutral}) - E(\text{anion at the neutral equilibrium geometry})$$

and (c) the vertical detachment energy of the anion

$$VDE = E(\text{neutral at the anion equilibrium geometry}) - E(\text{optimized anion})$$

Theoretical Methods

The DFT methods used here are based upon the self-consistent Kohn−Sham procedure.[27] The geometries and energies have been obtained utilizing four different gradient-corrected density functionals. The first, designated B3LYP, is a Hartree−Fock (HF)/DFT hybrid method that uses Becke's three-parameter functional (B3)[28] with Lee, Yang, and Parr's correlation functional (LYP).[29] The BHLYP method is also a HF/DFT hybrid method formed from Becke's half-and-half exchange functional (BH)[30] with the LYP correlation functional. The BLYP uses Becke's 1988 exchange functional (B)[31] with the LYP correlation functional. The fourth method, BP86, comprised the Becke (B) exchange functional with the correla-

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tion functional of Perdew (P86).[32] All these methods were used as implemented in the Gaussian 98 program package.[33] Throughout the computations, the default grid (75 302) was used for evaluating DFT integrals numerically and the tight (10^{-8} hartree) designation adopted for the self-consistent field (SCF) convergence.

The basis sets used here, denoted "DZP++", were standard double-ζ plus polarization (DZP) sets augmented with s and p diffuse functions. The DZP++ basis set for chlorine was constructed by using the Huzinage−Dunning−Hay standard double-ζ sp set[34] with d polarization functions [$\alpha_d(\mathrm{Cl}) = 0.75$] and augmented with s and p diffuse functions [$\alpha_s(\mathrm{Cl}) = 0.050\,48$ and $\alpha_p(\mathrm{Cl}) = 0.050\,87$]. The contraction scheme for chlorine is (12s8p1d/7s5p1d). For oxygen the corresponding basis set was composed of the standard Huzinage−Dunning double-ζ set[35] with one set of d polarization functions [$\alpha_d(\mathrm{O}) = 0.85$] as well as a set of diffuse [$\alpha_s(\mathrm{O}) = 0.082\,27$] and [$\alpha_p(\mathrm{O}) = 0.065\,08$] functions (10s6pld/5s3pld). The diffuse function orbital exponents were determined in an "even-tempered sense" as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer.[36] These diffuse functions enhance the ability to accurately describe the anions. All the geometries were determined to be minima via the evaluation of their harmonic vibrational frequencies at the same level of theory, unless otherwise indicated.

The DFT methods used here have been subjected to comprehensive tests with respect to their ability to predict electron affinities.[37] For a sample set of more than 100 experimental EAs, the B3LYP and BLYP methods had the lowest average absolute errors, namely 0.14 eV. However, the EA errors for the BP86 and BHLYP methods were also reasonable, 0.18 and 0.24 eV, respectively. The use of four independent DFT methods throughout also allows important internal consistency checks.

Results and Discussion

1. ClOO/ClOO$^-$. The first tentative identification of the short-lived neutral chlorine peroxide species ClOO was made in 1967 by Rochkind and Pimentel from the IR spectrum in rare gas matrixes.[38] In 1993 the definitive IR and UV spectra of the ClOO radical were recorded in matrix isolation.[16] Our theoretical equilibrium geometries for the ClOO ground state ($^2A''$) and the ClOO$^-$ $^1A'$ and $^3A''$ states are displayed in Figure 1. Both the ClOO and ClOO$^-$ species have bent structures with C_s symmetry. The electron configuration of the $^2A''$ ground state for the neutral ClOO radical is

$$(1-6a')^{12}1a''^{2}7a'^{2}8a'^{2}9a'^{2}10a'^{2}2a''^{2}11a'^{2}12a'^{2}3a''^{2}13a'^{2}4a''$$

while the electron configuration for the $^1A'$ state of the ClOO$^-$ anion is

$$(1-6a')^{12}1a''^{2}7a'^{2}8a'^{2}9a'^{2}10a'^{2}11a'^{2}2a''^{2}12a'^{2}13a'^{2}3a''^{2}4a''^{2}$$

and that of the $^3A''$ ground state is

$$(1-6a')^{12}1a''^{2}7a'^{2}8a'^{2}9a'^{2}2a''^{2}10a'^{2}11a'^{2}3a''^{2}12a'^{2}13a'^{2}4a''\,14a'$$

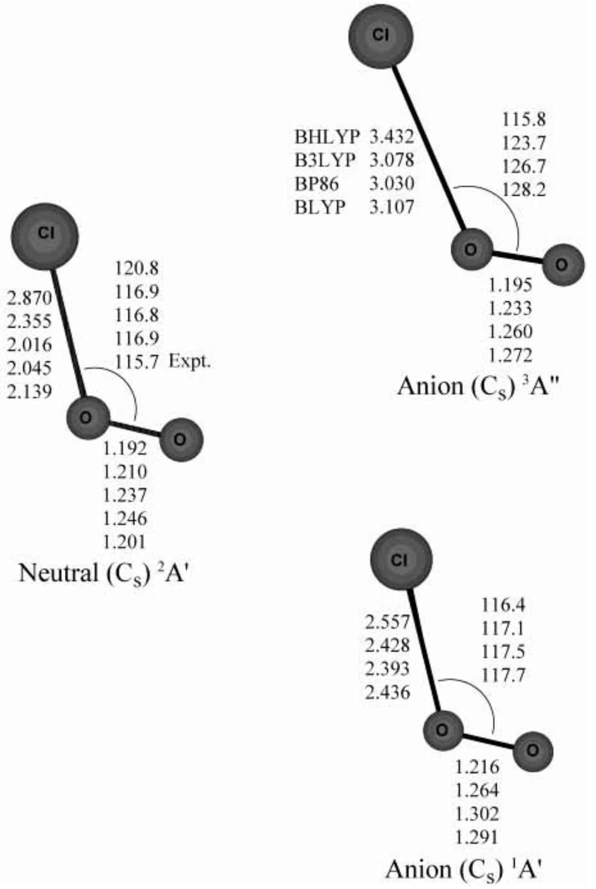

Figure 1. Molecular geometries of the $^2A'$ state of ClOO (C_s), and the $^1A'$ and $^3A''$ states of anionic ClOO$^-$ (C_s). Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

For the neutral ClOO $^2A''$ ground state, the Cl−O bond distance is predicted to be 2.016 (BP86) or 2.045 Å (BLYP). However, the Cl−O bond distances predicted by the hydrid BHLYP (2.870 Å) and B3LYP (2.355 Å) methods appear unreasonably long. For the normal C_{2v} symmetry ClO$_2$, the Cl−O bond distances predicted by the same methods are much shorter, namely 1.483 (BHLYP), 1.519 (B3LYP), 1.541 (BP86), and 1.558 (BLYP) Å.[25] The BHLYP and B3LYP results for ClOO also are highly suspect due to the large degrees of spin contamination, with $\langle S^2 \rangle = 1.742$ for BHLYP or 1.425 for B3LYP, indicating a significant higher spin state (primarily quartet state) contamination. The $^4A'$ and $^4A''$ states of ClOO have also been investigated, but both dissociate without a barrier to Cl and O$_2$. Conversely, for the pure DFT BLYP and BP86 methods the $\langle S^2 \rangle$ values are reasonably predicted to be 0.767 and 0.776, respectively. Therefore, only the BP86 and BLYP results for ClOO will be discussed hereafter. The fact that BHLYP and B3LYP lead to large spin contaminations was also noted in earlier work on the valence isoelectronic BrOO.[26] The O−O bond lengths for the ClOO neutral molecule are predicted to be 1.237 Å for BP86 and 1.246 Å for BLYP. The experimental structure of ClOO was reported by Müller[39] as 2.139 and 1.201 Å for the Cl−O and O−O bond distances, respectively. The experimental bond angle is 115.7°. Although the BP86 and BLYP methods predict somewhat shorter (by ∼0.1 Å) Cl−O bond and longer (by ∼0.04 Å) O−O bond distances than experiment, they predict reasonable geometries for ClOO. Compared with OClO, the ClOO isomer is lower in energy by 22.1 kcal/mol (0.96 eV) at the BP86 level of theory or 24.3 kcal/mol (1.05 eV) at BLYP. We note that a previous theoretical study of Beltran et al.[21] suggests that the energy difference was as small as 2.5 kcal/mol at the ROB3LYP/6-311+G(3df,2p) level. Of course, this difference is probably due in part to the use of rather different basis sets. In addition, as pointed out by Pople, Gill, and Handy, "Kohn−Sham theory, applied to open-shell systems, should be developed only in the

TABLE 1: Neutral−Anion Energy Separations and Harmonic Vibrational Frequencies for $ClOO(^2A'')/ClOO^-(^3A'')$

	EA_{ad} ClOO	EA_{vert} ClOO	VDE $ClOO^-$	vibr freq (cm^{-1}) ClOO (a′, a′, a′)	vibr freq (cm^{-1}) $ClOO^-$(a′, a′, a′)	ZPVE diff (eV) $ClOO/ClOO^-$
BHLYP	a	a	a	a	36, 48, 1798	a
B3LYP	a	a	a	a	64, 116, 1518	a
BP86	3.39	2.19	3.95	284, 502, 1423	58, 124, 1393	0.0014
BLYP	3.33	2.19	3.81	269, 481, 1377	52, 119, 1339	0.0014
expt				215, 432, 1478[39]		
				192, 408, 1443[16]		

[a] Due to the large spin contaminations for the neutral ClOO radical with the BHLYP and B3LYP methods, these results are not considered meaningful.

spin-unrestricted formalism (UKS). Spin restricted open shell formalisms (ROKS) should be avoided."[40] A much more reliable theoretical study on ClOO by Peterson and Werner[12] predicted that it lies 12.7 kcal/mol below OClO with the CMRCI(3d2f) method, even though the experimental value estimated by the same authors[12] is 4 kcal/mol. The unsymmetrical ClOO is certainly thermodynamically more stable than OClO among ClO_2 species.

For the $ClOO^-$ anion, the four DFT methods predict a closed-shell singlet ($^1A'$) state with Cl−O bond distance in the range from 2.393 (BP86) to 2.557 Å (BHLYP) and a lower energy triplet ($^3A''$) state with Cl−O bond distance from 3.030 (BP86) to 3.432 Å (BHLYP). The $^3A''$ structure could be regarded as a $Cl^-\cdots O_2$ complex, due to the significantly long Cl−O separation and the high negative atomic charge (from −0.99 to −0.80 with the four methods) on the Cl atom according to the population analysis. The $^3A''$ state lies energetically lower than the $^1A'$ state by as much as 37 kcal/mol at the DZP++ BHLYP level of theory. However, the $^3A''/^1A'$ energy difference was predicted to be lower, namely 26, 21, and 21 kcal/mol at the B3LYP, BP86, and BLYP levels of theory, respectively. Also, the $^3A''$ state of $ClOO^-$ is predicted to lie about 62, 54, 49, and 52 kcal/mol below the C_{2v} $OClO^-$ structure with the BHLYP, B3LYP, BP86, and BLYP levels of theory, respectively.

The $^1A'$ Cl−O bond distance in $ClOO^-$ is about 0.4 Å longer than that in its neutral counterpart (BP86 and BLYP). Also, the Cl−O−O bond angle of the $^1A'$ state increases a little, except for the BHLYP method. For the $^3A''$ ground state, the Cl−O bond distance is about 0.65 Å longer than that for the $^1A'$ state, except for the BHLYP result, which is about 0.88 Å longer. Also, the $^3A''$ O−O bond distance decreases by about 0.02 Å and the Cl−O−O bond angle increases by 10° compared to $^1A'$. Special note is made of the $^3A''$ Cl−O bond distance ordering, BHLYP > BLYP > B3LYP > BP86, which is different from the O−O bond distance trend, BHLYP < B3LYP < BP86 < BLYP.

Table 1 lists the adiabatic and vertical electron affinities for ClOO, as well as the vertical detachment energies for $ClOO^-$. These values have not been corrected by zero point vibrational energies (ZPVE) because the ZPVE corrections are quite small, as shown in the far right column of Table 1. The EA_{ad} is predicted to be 3.39 eV (BP86) and 3.33 eV (BLYP). The values of EA_{vert} for ClOO are about 1.2 eV smaller than those for EA_{ad}, while the VDE of $ClOO^-$ is about 0.46 eV larger. The differences of course reflect the different equilibrium geometries of ClOO and $ClOO^-$. Compared with its OClO isomer,[25] the EA_{ad} of the ClOO isomer is about 1.2 eV larger.

Table 1 also contains predictions of the harmonic vibrational frequencies for ClOO and the $ClOO^-$ triplet state. The harmonic vibrational frequencies determined by BP86 and BLYP methods are in reasonably good agreement with the experimental matrix data.[16,39]

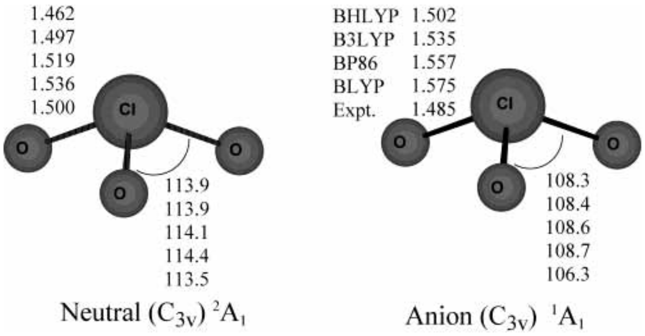

Figure 2. Molecular geometries of the $^2A_1$ state of ClO_3 (C_{3v}) and the $^1A_1$ state of anionic ClO_3^- (C_{3v}). Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

2. ClO_3/ClO_3^-. In 1994 Grothe and Willner[17] reported the first experimental evidence for ClO_3, through the vacuum flash photolysis of chlorine perchlorate Cl_2O_4 and matrix isolation of the products. Our theoretical C_{3v} symmetry equilibrium geometries for the X $^2A_1$ state of ClO_3 and the X $^1A_1$ state of ClO_3^- are shown in Figure 2. The electron configuration for the $^2A_1$ neutral molecule ground state is

$$(1-4a_1)^8(1-2e)^8 5a_1^{\,2} 3e^4 6a_1^{\,2} 7a_1^{\,2} 4e^4 5e^4 6e^4 1a_2^{\,2} 8a_1$$

while the $^1A_1$ anion has a second electron added to the $8a_1$ orbital. The bond length predictions of the four functionals for ClO_3 are in the range of 1.46−1.54 Å and those for ClO_3^- fall in the range 1.50−1.58 Å following the same trends as ClO and OClO.[25] The experimental structure for ClO_3 was reported by Grothe and Willner[17] as 1.50 ± 0.01 Å and 113.5° ± 2° for the Cl−O bond distance and the O−Cl−O bond angle, respectively. The neutral structure predicted by the B3LYP method is the closest to experiment.

An excited electronic state ($^2A_2$) for neutral ClO_3 of C_{3v} symmetry was found to lie 6−12 kcal/mol above the ground state $^2A_1$ with the four theoretical methods. The Cl−O bond length for this state is predicted to be in the range of 1.52−1.56 Å, and the O−Cl−O bond angle is predicted to be 104.6°−105.3°. The C_{3v} symmetry structure of the excited $^2A_2$ state is more pyramidal than the $^2A_1$ structure and has a longer ClO bond distance. All four theoretical methods predict that the $^2A_2$ state has a doubly degenerate imaginary vibrational frequency (OClO bending e mode). Rauk et al.[13] in 1993 reported theoretical $^2A_1$ and $^2A_2$ structures for ClO_3 with the UHF, ROHF, UMP2, and ROMP2 methods. With the 6-31G(d) basis set both structures are minima, but on the QCISD(T)/6-31G(d) surface the curvature is qualitatively different, with a doubly degenerate imaginary vibrational frequency. The QCISD(T) results of Rauk et al. are in agreement with the present theoretical study.

TABLE 2: Neutral−Anion Energy Separations and Harmonic Vibrational Frequencies for ClO_3/ClO_3^-

	EA_{ad} (eV) ClO_3	EA_{vert} (eV) ClO_3	VDE (eV) ClO_3^-	vibr freq (cm^{-1}) ClO_3 (e, a_1, a_1, e)	vibr freq (cm^{-1}) ClO_3^- (e, a_1, a_1, e)	ZPVE diff (eV) ClO_3/ClO_3^-
BHLYP	4.37	3.81	5.03	481, 556, 946, 1073	471, 598, 953, 1014	0.0002
B3LYP	4.29	3.81	4.78	432, 512, 857, 965,	424, 544, 870, 911	0.0002
BP86	4.07	3.62	4.38	401, 487, 811, 923	393, 510, 824, 864	0.0002
BLYP	3.97	3.56	4.24	385, 468, 763, 849	376, 486, 777, 807	0.0002
expt	>3.2[42]			476, 567, 905, 1081[17]		

The bond lengths for the ClO_3^- anion are predicted to be longer than those for its neutral counterpart by about 0.04 Å, and the O−Cl−O anion bond angle is smaller than the neutral by about 4.5°. For the ClO_3^- anion, there are no gas-phase experimental data, but X-ray structures for barium chlorate monohydrate $Ba(ClO_3)_2 \cdot H_2O$ and potassium chlorate $KClO_3$ are available for comparison.[41,42] The BHLYP method gives the shortest Cl−O bond distance, which is the nearest that of the ClO_3^- crystal structure in $Ba(ClO_3)_2 \cdot H_2O$. The BHLYP result for the Cl−O bond distance is about 0.02 Å longer than that for the crystal structure.

The theoretical EA_{ad}, EA_{vert}, and VDE values are listed in Table 2. The range for EA_{ad} is from 3.97 to 4.37 eV, the range for EA_{vert} is from 3.56 to 3.81 eV, and that for VDE is from 4.24 to 5.03 eV. All four functionals predicted the value of the EA_{ad} to be larger than the only experimental value (>3.2 eV), a lower limit.[42]

The harmonic vibrational frequencies of ClO_3/ClO_3^- are also presented in Table 2. The BHLYP method gives the highest frequencies (closest to the available experimental results), while BLYP gives the lowest.

3. ClOOO/ClOOO$^-$. Although there is no experimental detection reported to date for the ClOOO isomer, Beltran et al.[21] have predicted the energy of this isomer to be lower than that of the C_{3v} isomer by 22 kcal/mol at the spin-restricted ROB3LYP/6-311+G(3df,2p) level. Rauk et al.[13] found the C_s ClOOO structure to be a transition state at the RMP2 and QCISD(T) levels of theory. However, the ROB3LYP calculations of Janoschek[43] conclude in favor of ClOOO being a minimum.

For the unrestricted open-shell doublet state ClOOO system, our BHLYP and B3LYP results, as with the case of ClOO, had serious spin contamination ($\langle S^2 \rangle = 1.774$ and 1.728 for BHLYP and B3LYP, respectively). Furthermore, the distances between the two middle oxygen atoms for both trans and cis structures predicted with BHLYP and B3LYP are too long (∼3 Å). This is similar to the UB3LYP/ 6-311+G(3df,2p) results published by Beltran et al.,[21] who suggest one imaginary frequency due to the spin contamination effect. The results of the structure optimizations carried out with the other two DFT functionals are given in Figure 3. The fainter structures are BHLYP and B3LYP geometries, which have at least educational value, but we will not use the BHLYP and B3LYP results for ClOOO in further discussions because of the serious spin contamination effect. There are two minimum energy structures, cis and trans, for the neutral doublet ClOOO system at the BLYP and BP86 levels of theory. Their electronic ground states are both $^2A''$. The ground-state *cis*-ClOOO is predicted to lie below *trans*-ClOOO by 4.7 (BP86) or 4.0 (BLYP) kcal/mol. For the *cis*-ClOOO conformer the ClO−OO distances are predicted to be 1.842 and 1.871 Å for BP86 and BLYP, respectively, which is about 0.05 Å longer than for the *trans*-ClOOO conformer. The *cis*-ClOOO structure agrees qualitatively with the previous theoretical results reported by Beltran et al. with the ROB3LYP method.[21] However, in our DFT predictions, the *cis*-ClOOO isomer has a lower energy than ClO_3 (C_{3v}) by 53 (BP86) and 57 (BLYP) kcal/mol, a separation which is much larger than the ROB3LYP/6-311+G(3df,2p) results.[21] This is not entirely unexpected, since, as noted by Pople, Gill, and Handy,[40] the restricted open-shell Kohn−Sham formalism should be treated with caution.

For the anionic ClOOO$^-$ system, there are three minima for the singlet state: the *trans*-, *cis*-, and *gauche*-ClOOO$^-$ structures, presented in Figure 3. The bond length order predicted by the four DFT methods is the same as the order for neutral ClO_3. The energy of the *gauche*-ClOOO$^-$ ^1A state is lower than that of the *cis*-ClOOO$^-$ $^1A'$ state by 11−24 kcal/mol for the four functionals, and the cis singlet structure lies about 1 kcal/mol lower in energy than the trans singlet. This gauche structure could be regarded as $Cl^- \cdots O_3$ complex because of the significantly long (∼2.5 Å) separation and the high negative atomic charge (from −0.73 to −0.60 with the four methods) on the Cl atom. However, the cis and trans singlet structures look like $ClO^- \cdots O_2$ complexes. We expect the triplet state for $ClO^- \cdots O_2$ to possess a lower energy. Indeed, there are four $^3A''$ ClOOO$^-$ conformers (Figure 4). Two of these (bottom two structures in Figure 4) have the $Cl^- \cdots O_3$ structure (cis and trans) with higher energies, and the cis has higher energy than the trans by 3−4 kcal/mol (Table 3). The other two (top two in Figure 4, also cis and trans) with the $ClO^- \cdots O_2$ structure lie lower in energy, and the cis has a lower energy than trans by ∼0.1 kcal/mol (Table 3). Surprisingly, the BHLYP and B3LYP methods predict quite different (*as large as 30*°) bond angles for the $^3A''$ cis $ClO^- \cdots O_2$ structure from the BP86 and BLYP methods (Figure 4). Also, the relative energies of the $^3A''$ cis $ClO^- \cdots O_2$ structure, with respect to the gauche ^1A structure, predicted by the BHLYP and B3LYP methods are accordingly quite different from those by the BP86 and BLYP methods. The gauche structure lies higher in energy than the cis by 18 kcal/mol predicted by BHLYP, but lies lower by 8−11 kcal/mol predicted by BP86 and BLYP (Table 3). Considering that the BHLYP and B3LYP methods do poorly for the neutral ClOOO system, we will hereafter use only the results from BP86 and BLYP and take the gauche ClOOO$^-$ structure as the global minimum.

Energetically, *gauche*-ClOOO$^-$ lies below ClO_3^- (C_{3v}) by 7.7 (BHLYP), 21.2 (B3LYP), 26.2 (BP86), and 31.4 (BLYP) kcal/mol. This energy difference is smaller than that between the neutral ClO_3 and ClOOO isomers. Consequently, the EA for ClOOO will be smaller than that of ClO_3. The EA_{ad}, EA_{vert}, and VDE values are shown in Table 4. The EA_{vert} and VDE are quite different from EA_{ad} due to the significant geometric changes in the global minima betweem ClOOO and ClOOO$^-$.

The theoretical harmonic vibrational frequencies of ClOOO and its anion are presented in Table 4. To date, no experimental data are available for comparison.

4. Dissociation Energies. The Cl−O bond dissociation energies for neutral ClO_n ($n = 1-4$) are shown in Table 5. They are determined as the energy differences for the reactions $ClO_n \rightarrow ClO_{n-1} + O$.

For diatomic ClO the experimental dissociation energy is 2.75 eV.[44] Note that the B3LYP method with the DZP++ basis set gives the best estimation (2.57 eV), while the BHLYP method

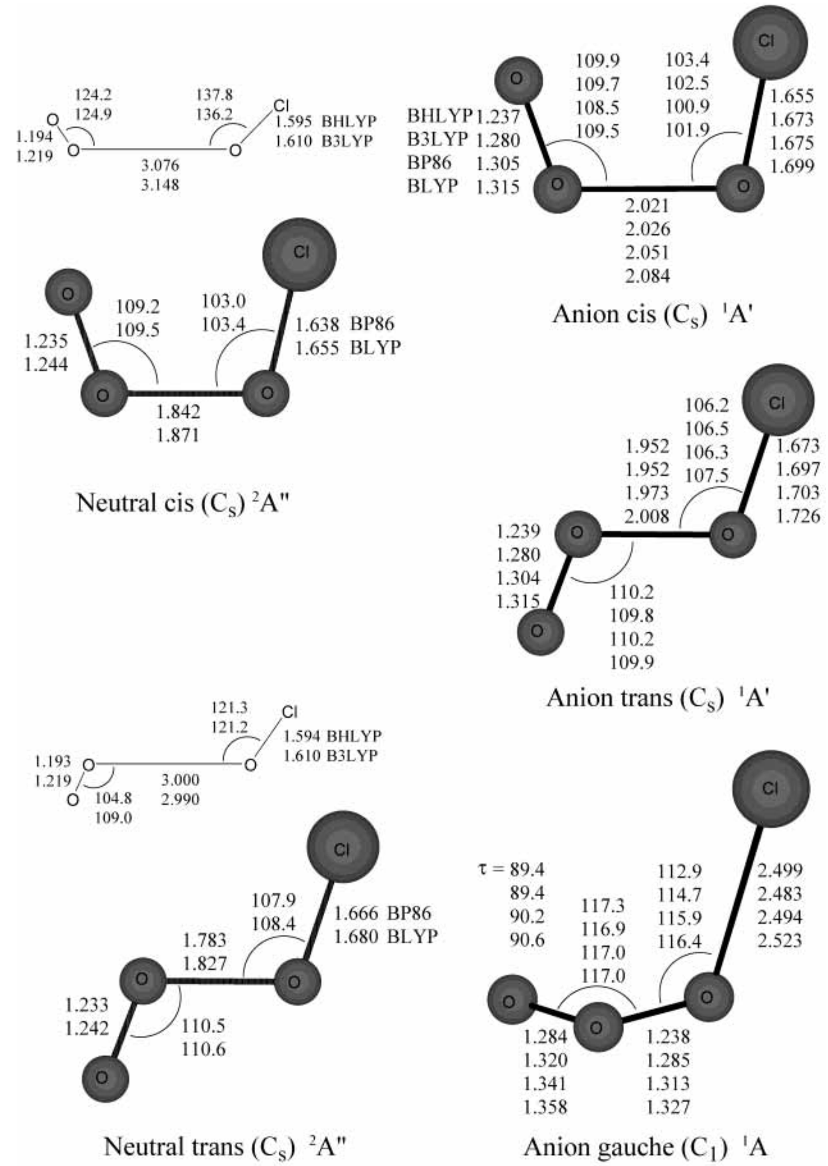

Figure 3. Molecular geometries of the $^2A''$ states of *cis*-ClOOO and *trans*-ClOOO, and the singlet state of anionic $ClOOO^-$. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

gives only 1.87 eV (Table 5). For ClO_2, the derived experimental D_0 is 2.63 eV,[45,46] and the pure DFT methods BP86 and BLYP predict better results (2.62 and 2.33 eV) than the hybrid HF/DFT methods BHLYP and B3LYP (0.68 and 1.72 eV). The BP86 method gives a D_e value with an error of only 0.01 eV, which should be considered fortuitously good for thermochemical predictions. For ClO_3 and ClO_4, there are no reliable experimental data for comparison, but we conclude that the BP86 and BLYP results are more reliable than those from BHLYP and B3LYP. As a matter of fact, the BHLYP and B3LYP results are much smaller than those given by BP86 and BLYP, the same trend as that found for ClO and ClO_2 (Table 5). For ClOO and ClOOO, there are no meaningful results for the BHLYP and B3LYP methods, due to the serious spin contamination. The D_e values for ClOO at the BP86 and BLYP levels of theory are 3.58 and 3.38 eV, respectively. These dissociation energies are larger than those for ClO_2 because ClOO lies lower in energy. For ClOOO, the BP86 and BLYP dissociation energies are 2.81 and 2.62 eV, respectively, which are also larger than those for symmetric ClO_3.

The predicted bond dissociation energies for the anionic ClO_n^- ($n = 1-4$) species are shown in Table 6. There are two kinds of dissociation processes, which are defined as $ClO_n^- \rightarrow ClO_{n-1} + O^-$ and $ClO_n^- \rightarrow ClO_{n-1}^- + O$. The experimental D_0 are derived from the heats of formation of the reactant and products.[14,42,45,47-49] All anions ClO_n^- studied are predicted to be thermodynamically stable with respect to dissociation. The dissociation energies to oxygen atom are smaller than those to oxygen anion, indicating that the dissociation to the neutral oxygen atom is favored.

Conclusions

Following our previous theoretical work on ClO, ClO_2, and ClO_4,[24,25] we report two minima for ClO_3, locate the ground state for ClO_2, and examine the pertinent anions with four independent DFT methods. Although we find the BHLYP method usually seems to be the preferred DFT method for the prediction of the molecular geometries, the BHLYP and B3LYP methods are not appropriate for the doublet ClOO and ClOOO species, due to large spin contaminations, while the BLYP and BP86 methods give reasonable $\langle S^2 \rangle$ expectation values (<0.76). The predicted adiabatic electron affinities with the favored BLYP method are 3.33 eV for ClOO, 3.97 eV for ClO_3, and

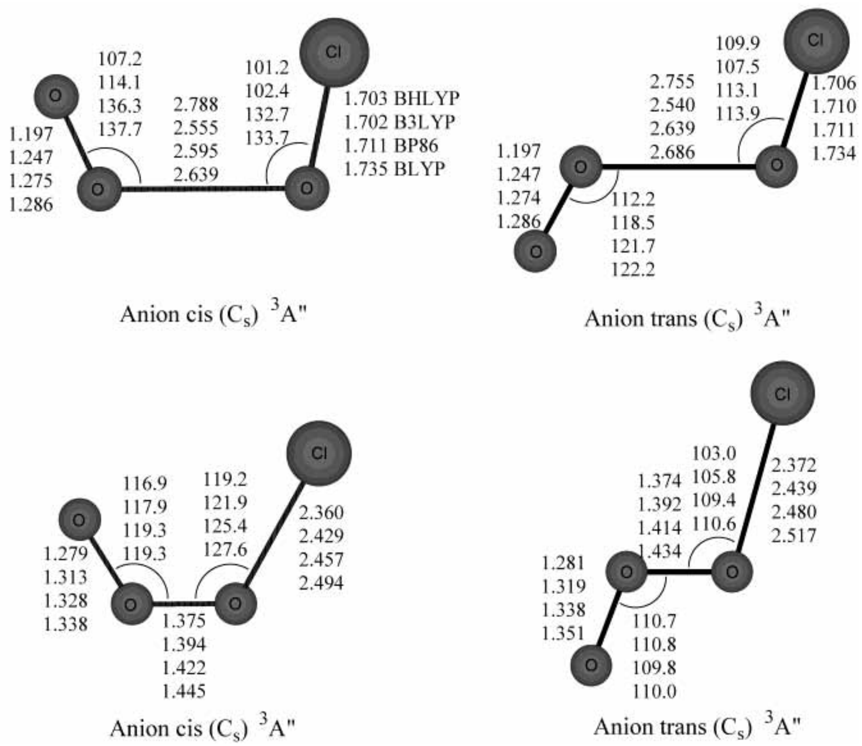

Figure 4. Molecular geometries of the triplet $^3A''$ state of anionic $ClOOO^-$ (C_s). Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

TABLE 3: Relative Energies (kcal/mol) for the Conformers of $ClOOO^-$

	gauche-$Cl^-\cdots OOO$ ^1A	*cis*-$ClO^-\cdots OO$ $^3A''$	*trans*-$ClO^-\cdots OO$ $^3A''$	*cis*-$Cl^-\cdots OOO$ $^3A''$	*trans*-$Cl^-\cdots OOO$ $^3A''$	*cis*-$ClO^-\cdots OO$ ^1A	*trans*-$ClO^-\cdots OO$ ^1A
BHLYP	0.0	−17.8	−17.8	−4.1	−8.6	11.3	12.5
B3LYP	0.0	−0.6	−0.4	6.4	2.6	18.1	19.3
BP86	0.0	10.7	10.8	13.5	10.1	24.4	26.0
BLYP	0.0	8.1	8.3	11.6	8.3	23.1	24.1

TABLE 4: Neutral−Anion Energy Separations and Harmonic Vibrational Frequencies for *cis*-ClOOO/*gauche*-$ClOOO^-$

	EA_{ad} (eV) ClOOO	EA_{vert} (eV) ClOOO	VDE (eV) $ClOOO^-$	vibr freq (cm^{-1}) *cis*-ClOOO (a′, a″, a′, a′, a′, a′)	vibr freq (cm^{-1}) *gauche*-$ClOOO^-$ (a, a, a, a, a, a)	ZPVE diff (eV) ClOOO/$ClOOO^-$
BHLYP	a	a	4.01	a	107, 185, 301, 746, 1193, 1386	a
B3LYP	a	a	4.70	a	108, 197, 301, 676, 1082, 1156	a
BP86	2.93	1.58	4.55	195, 243, 390, 543, 800, 1462	104, 195, 289, 634, 956, 1062	0.0009
BLYP	2.84	1.55	4.40	182, 230, 365, 518, 766, 1416	101, 188, 279, 610, 898, 1019	0.0009

[a] Due to the large spin contaminations for the neutral ClOOO radical with the BHLYP and B3LYP methods, these results are not considered meaningful.

TABLE 5: Bond Dissociation Energies (eV) for Neutral ClO_n Species[a]

	BHLYP	B3LYP	BP86	BLYP	expt
$ClO \rightarrow Cl + O$	1.87	2.57	3.15	2.96	2.75[44]
ClO_2 (C_{2v}) $\rightarrow ClO + O$	0.68	1.72	2.62	2.33	2.63[45,46]
ClO_3 (C_{3v}) $\rightarrow ClO_2 + O$	0.14	0.81	1.49	1.19	
$ClO_4 \rightarrow ClO_3 + O$	0.81	1.22	1.78	1.46	
$ClOO \rightarrow ClO + O$	b	b	3.58	3.38	
$ClOOO \rightarrow ClOO + O$	b	b	2.81	2.62	

[a] The experimental dissociation energies D_0 are derived from the related heats of formation. [b] Due to the large spin contaminations for the neutral ClOO and ClOOO radicals with the BHLYP and B3LYP methods, these results are not considered meaningful.

TABLE 6: Bond Dissociation Energies (eV) for the Anion ClO_n^- Species[a]

	BHLYP	B3LYP	BP86	BLYP	expt
$ClO^- \rightarrow Cl + O^-$	2.82	3.18	3.54	3.32	3.60[14,45,49]
$ClO_2^- \rightarrow ClO + O^-$	2.03	2.47	2.96	2.68	3.46[14,45,49]
$ClO_3^- \rightarrow ClO_2 + O^-$	3.40	3.44	3.68	3.36	4.10[42,45,49]
$ClO_4^- \rightarrow ClO_3 + O^-$	5.13	4.87	4.92	4.51	
$ClOO^- \rightarrow ClO + O^-$	4.73	4.82	5.09	4.92	
$ClOOO^- \rightarrow ClOO + O^-$	b	b	2.80	2.67	
$ClO^- \rightarrow Cl^- + O$	0.42	1.10	1.58	1.48	1.45[14,45,48]
$ClO_2^- \rightarrow ClO^- + O$	1.07	1.86	2.57	2.33	2.64[14,45]
$ClO_3^- \rightarrow ClO_2^- + O$	2.06	2.69	3.35	3.01	3.19[14,42,45]
$ClO_4^- \rightarrow ClO_3^- + O$	1.86	2.25	2.73	2.34	3.90[42,45,47]
$ClOO^- \rightarrow ClO^- + O$	3.78	4.21	4.70	4.57	
$ClOOO^- \rightarrow ClOO^-$ ($^3A''$) + O	−0.80	0.47	1.30	1.13	
$ClOOO^- \rightarrow ClOO^-$ ($^1A'$) + O	0.79	1.60	2.19	2.02	

[a] The experimental dissociation energies D_0 are derived from the related heats of formation. [b] Due to the large spin contaminations for the neutral ClOO radical with the BHLYP and B3LYP methods, these results are not considered meaningful.

2.84 eV for ClOOO. The predicted ground states of $ClOO^-$ and $ClOOO^-$ are triplet ($^3A''$) and *gauche*-$ClOOO^-$ (^1A), respectively. These may be regarded as $Cl^-\cdots O_2$ and $Cl^-\cdots O_3$ complexes.

Dissociation energies obtained at different theoretical levels for ClO_n ($n = 1-4$) show a steady progression in the order BHLYP < B3LYP < BLYP < BP86 (Tables 5 and 6). Taking into account that our best estimates of known thermochemistry for related compounds are from the pure DFT BLYP and BP86 methods, we conclude that our most reliable results in the prediction of the dissociation energies are expected from the BLYP and BP86 methods. Note also that the BLYP method with the DZP++ basis set gives our best estimate of electron affinities of ClO and ClO_2.[25] The BLYP is thus considered to be our most reliable for the EA prediction of ClOO, ClOOO and ClO_3.

This present research may be viewed as a road map for future theoretical and experimental studies. Although it is clear that the electron affinities of ClOO, ClO_3, and ClOOO are substantial, further research will be necessary to achieve chemical accuracy of 1 kcal/mol (0.04 eV). The same is true of the predicted dissociation energies.

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