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# Ab initio characterization of the weakly bound anions $ClOO^-$ and $ArCl^-$

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## Abstract

Experimental studies of the energetics and vibrational spectrum of the chloroperoxyl radical, ClOO, are contradictory. The most recent experiment accessed the radical by photodetachment of the corresponding anion, $ClOO^-$. The present study uses both multi- and single-configuration ab initio methods to characterize various structures and spin-states of the ion. The calculations support the recent experimental description of $ClOO^-$ as a weakly bound complex, not a chloroperoxide anion. Two local minima (bent and linear) were found on the triplet-state potential energy surface; the lower has an average equilibrium Cl–O distance of 359 pm and equilibrium Cl–O–O bond angle of 96°. However, the vibrational ground state has $C_{2v}$ symmetry, resulting in the designation $^3B_1$ for the electronic ground state. The singlet excited state is asymmetric and lies near $T_e(\tilde{a}^1A') = 7895\,\mathrm{cm}^{-1}$. The calculated binding energy is $D_0(Cl^-–O_2) = 478 \pm 10\,\mathrm{cm}^{-1}$ ($5.72 \pm 0.12\,\mathrm{kJ\,mol}^{-1}$), corresponding to an ideal-gas enthalpy of formation of $\Delta_f H_0^\circ(ClOO^-) = -234.80 \pm 0.23\,\mathrm{kJ\,mol}^{-1}$. Small Franck–Condon factors are expected for adiabatic electron detachment, in conflict with the vertical process inferred from the experiments. Thus, the experimentally determined electron affinity is only an upper limit. Companion calculations on $ArCl^-[D_0(Cl^-–Ar) = 489\,\mathrm{cm}^{-1}]$ support both experimental estimates $[D_0(Cl^-–Ar) = 494 \pm 5\,\mathrm{cm}^{-1}]$ and the present calculations for $ClOO^-$.

*Keywords:* Ab initio; Argon chloride; Chlorine dioxide; Electron affinity; Isomer; Thermochemistry; van der Waals

## 1. Introduction

A recent study of $ClOO^-$, using high-resolution photoelectron spectroscopy (ZEKE-PES), revealed a number of basic characteristics of the ion [1]. The electron affinity was determined as $EA(ClOO) = 3.6600 \pm 0.0002\,\mathrm{eV}$, close to the value for the free chlorine atom, $EA(Cl) = 3.61273 \pm 0.00003\,\mathrm{eV}$ [2]. The two principal bands are separated by $899.8\,\mathrm{cm}^{-1}$, close to the term-splitting in the free chlorine atom, $882.35\,\mathrm{cm}^{-1}$ [3]. Both were assigned as vibrational origins. From hot bands, a vibrational fundamental in the anion was measured as $46.8\,\mathrm{cm}^{-1}$. A Birge–Sponer extrapolation suggested that the binding energy is only $D_0(Cl^-–O_2) = 6.7\,\mathrm{kJ\,mol}^{-1}$. Thus, $ClOO^-$ appears to be a weakly bound complex between $Cl^-$ and $O_2$.

Information about the neutral molecule, ClOO, was also obtained from the experiments. A vibrational fundamental of $24.5\,\mathrm{cm}^{-1}$ ($24.1\,\mathrm{cm}^{-1}$ in the upper spin-orbit level) was obtained. Birge–Sponer extrapolation provided the dissociation energy $D_0(Cl^-–O_2) = 2.0\,\mathrm{kJ\,mol}^{-1}$ ($2.8\,\mathrm{kJ\,mol}^{-1}$ in the

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upper spin-orbit level). These results, plus the general similarity of the spectrum to that of $ArCl^-$, led the authors to conclude that neutral ClOO is also a weakly bound, van der Waals complex [1]. They noted that their value for the dissociation energy is markedly lower than earlier experimental values: $19.9 \pm 2.1\,kJ\,mol^{-1}$ [4], $20.2 \pm 0.2\,kJ\,mol^{-1}$ [5], and $19.2 \pm 1.7\,kJ\,mol^{-1}$ [6]. To rationalize this discrepancy, they speculated that their photodetachment experiment accesses a different structure of ClOO than that in the earlier experiments.

The PE spectrum is determined by the properties of both the lower (anion) and upper (neutral) states, but independent information is available in the literature only for neutral ClOO. The purpose of the present work is to use high-level ab initio calculations to investigate the structure of the $ClOO^-$ ion, to either support or dispute the conclusions from the recent experimental study.

After this manuscript was submitted for publication, a density-functional (DFT) study of $ClOO^-$ appeared [7]. Although quantitative results for a weakly bound molecule are not expected from DFT [8–10], it did predict, correctly, that the ground state is a triplet and is best described as a complex between $Cl^-$ and $O_2$. Numerical comparisons with DFT are made in the text and tables.

## 2. Computational methods

Geometries and harmonic vibrational frequencies were calculated using diffuse basis sets to accommodate the negative charge: aug-cc-pVTZ [11,12] on oxygen and aug-cc-pV(T+d)Z [13,14] on chlorine and argon. Taken together, this basis will be denoted aug-cc-pV(T+d)Z here. Single-reference calculations are generally inadequate to describe the singlet states of oxygen, a biradical. Thus, multireference calculations were used to compare singlet and triplet states of $ClOO^-$. The active space (8, 6) consisted of the oxygen 2p orbitals only. Large active spaces, such as full-valence (20, 12), gave problems with orbital flipping, in which oxygen K-shell orbitals became active and valence orbitals of $Cl^-$ became inactive. Both self-consistent field (CASSCF) and second-order perturbation (MCQDPT2 [15]) theories were used. The seven core orbitals were left uncorrelated in the MCQDPT2 calculations. The GAMESS program [16,17] was used for all multireference calculations (175 contracted Cartesian basis functions). In the non-gradient, MCQDPT2 geometry optimizations, the geometry convergence criteria were tightened to the values suggested in the GAMESS manual.

Triplet states were also characterized using frozen-core coupled-cluster theory [CCSD(T)] with a spin-unrestricted self-consistent (UHF) reference. The ACES II program suite [18] was used for all coupled-cluster and most other single-reference calculations (147 contracted spherical basis functions), with the basis-set linear-dependency threshold relaxed to accept overlap eigenvalues as small as $10^{-6}$. The CCSD(T) geometry convergence criterion was tightened from the default value of $10^{-4}$ to $10^{-6}$ a.u. ($1\,a.u. = 4148\,cm^{-1}\,pm^{-1}$). Tight convergence is generally necessary when there is a totally symmetric vibration of very low frequency, as for $ClOO^-$ in the $^3A''$ case; the Cl–O distance increases by 5.1 pm and bond angle decreased by 6.4° when the convergence criterion was tightened.

The suitability of these theoretical methods was evaluated by using the isolated oxygen molecule ($X^3\Sigma_g^-$ and $a^1\Delta_g$) as a test system. The results for bond length, harmonic vibrational frequency, and excitation energy are summarized in Table 1. The good agreement with experimental values indicates that the methods are appropriate. At the MCQDPT2 level, analytical gradients are lacking and there is no provision in the software for non-gradient frequency calculations. Nonetheless, the harmonic vibrational frequency was computed (solving for $v = 0, 1, 2$ using the Fourier-grid Hamiltonian method [19,20]) for completeness of Table 1. The CCSD(T) results for singlet $O_2$ are also included for completeness, although the corresponding excitation energy is clearly too high. The calculations of geometries and vibrational frequencies were uncorrected for BSSE.

Table 1
Test calculations on the $O_2$ molecule (aug-cc-pVTZ basis)

| Method | $X^3\Sigma_g^-$ | | $a^1\Delta_g$ | | |
|---|---|---|---|---|---|
| | $r_e$ (pm) | $\omega_e$ ($cm^{-1}$) | $r_e$ (pm) | $\omega_e$ ($cm^{-1}$) | $T_e$ ($cm^{-1}$) |
| Expt. [44] | 120.75 | 1580.2 | 121.56 | 1509 [45] | 7918.1 |
| CASSCF(8, 6) | 121.6 | 1541 | 122.9 | 1453 | 7142 |
| MCQDPT2(8, 6) | 122.0 | 1537 | 122.9 | 1462 | 8149 |
| CCSD(T) | 121.3 | 1574 | 122.5 | 1474 | 10408 |

Three procedures were considered for computing the binding energy of this weakly bound complex: (1) energy differences corrected for basis-set superposition error (BSSE) using a counterpoise correction [21], (2) energy differences calculated with the atomic basis sets supplemented by a set of bond functions [22], or (3) energy differences extrapolated to the limit of a complete one-electron basis set, with or without explicit correction for BSSE (which extrapolates to zero) [23,24]. The first option was rejected because the affordable basis sets are too small to provide a converged result. The second option was rejected because of arbitrariness regarding the position of the center(s) of the bond functions, and because the corresponding basis set would have to be developed. The third option was chosen because a good result can be expected and the procedure is well defined.

Equilibrium binding energies $D_e(Cl^-–O_2)$ were computed as the energy difference between $ClOO^-$ and its dissociated fragments, $Cl^-$ and $O_2$, all at their frozen-core CCSD(T)/aug-cc-pV(T+d)Z geometries. Energies were computed using the aug-cc-pV$n$Z basis set on oxygen and the corresponding aug-cc-pV($n$+d)Z basis sets on chlorine and argon, where $n = 3$(T), 4(Q), 5, 6, as devised by Dunning and co-workers [23]. For $ClOO^-$, these basis sets have 147, 249, 390, and 576 contracted spherical Gaussian functions, respectively. For $ArCl^-$, the corresponding counts are 110, 178, 272, and 396. Dissociation energies were extrapolated to the limit of a complete one-electron basis. The limiting value at the Hartree–Fock (UHF) level was not extrapolated, but was taken to be equal to the value obtained using the $n = 6$ basis sets, as recommended by Halkier et al. [25]. The difference in binding energy obtained by including correlation energy was extrapolated assuming the behavior given by Eq. (1) [26]. Rearrangement to a more convenient form gives Eq. (2). The correlation contribution to $D_e$

$$E_n = E_\infty + An^{-3} \tag{1}$$

$$E_\infty \frac{cE_{n+1} - E_n}{c - 1}, \quad c \equiv \frac{(n+1)^3}{n^3} \tag{2}$$

was broken into an MP2 part and an additional increment for CCSD(T), instead of a CCSD part and a (T) part as is more often done [27]. Since Eq. (2) is linear, the result obtained does not depend upon how the correlation contributions are partitioned (for equal $n$). However, the present procedure has the advantage that MP2 calculations are feasible for larger basis sets (i.e., larger $n$) than are CCSD calculations. Surprisingly and fortunately, the difference between CCSD(T) and MP2 also shows equal or faster convergence with basis set than does the difference between CCSD(T) and CCSD, at least for these systems. The extrapolation procedure was repeated using binding energies corrected for BSSE by the counterpoise method [21]. The BSSE-corrected results are preferred as more theoretically rigorous. The Gaussian 98 program[1] [28] was used for the larger SCF and MP2 calculations, with the automatic elimination of basis-set linear dependencies turned off, and was used for all DFT calculations. An integration grid finer than the default appears to be necessary for obtaining reasonable energies in the DFT calculations. For example, the counterpoise

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[1] Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

correction for $ArCl^-$ has the wrong sign when using the default grids. The DFT calculations done for the present study used the pruned "ultrafine" grid [28].

Thermodynamic binding energies $D_0(Cl^-–O_2)$ were computed by correcting the equilibrium binding energies for the vibrational zero-point energy (ZPE) of the molecule and the fragments. ZPEs were computed as one-half the sum of the harmonic vibrational frequencies, without scaling, from frozen-core CCSD(T)/aug-cc-pV(T+d)Z calculations. Bond enthalpy corrections for temperatures above zero were not attempted because the vibrations are expected to be strongly non-harmonic and only a harmonic vibrational analysis is included in the present study.

## 3. Results

The weakly bound anion $ArCl^-$ was chosen for testing computational procedures, since it has been relatively well characterized experimentally. $ArCl^-$ can be described using single-reference methods. Its geometry and harmonic vibrational frequency, computed at the frozen-core CCSD(T)/aug-cc-pV(T+d)Z level, are $r_e = 371.7\,\text{pm}$ and $\omega_e = 52.0\,\text{cm}^{-1}$ (so $\text{ZPE} = 26.0\,\text{cm}^{-1}$). The total energies calculated for $ArCl^-$, Ar, and $Cl^-$ are listed in Table 2. Detailed results of the counterpoise calculations are available from the author upon request. The corresponding equilibrium binding energies, $D_e(Ar–Cl^-)$, are listed in Table 3 both with and without corrections for BSSE. As described above, the basis-set limit for the HF binding energy is taken to be the value obtained using the $n = 6$ basis sets. The increments to $D_e$ due to correlation at the MP2 level, and subsequently at the CCSD(T) level, are also included in Table 3. The increments were extrapolated to the limit of a complete basis set ($n = \infty$) using Eq. (2) and the largest basis sets for which calculations were feasible. The total binding energy (Table 3) is thus calculated to be $D_e = 514.9\,\text{cm}^{-1}$. After correcting for $\Delta\text{DZPE} = -26.0\,\text{cm}^{-1}$, $D_0(Ar–Cl^-) = 488.9\,\text{cm}^{-1}$ ($495.3\,\text{cm}^{-1}$ without the BSSE corrections). Since coupled-cluster calculations with the $n = 5$ basis sets were not feasible for $ClOO^-$, the effect of

Table 2
Total energies (in Hartree) for $ArCl^-$, $ClOO^-$, and their fragments

| $n$[a] | Species | HF | MP2[b] | CCSD[b] | CCSD(T)[b] |
|---|---|---|---|---|---|
| 3 | $ArCl^-$ | −986.387413 | −986.809179 | −986.842203 | −986.859933 |
| | Ar | −526.813352 | −527.025406 | −527.043426 | −527.051151 |
| | $Cl^-$ | −459.573481 | −459.781540 | −459.796846 | −459.806626 |
| 4 | $ArCl^-$ | −986.393731 | −986.855329 | −986.887008 | −986.907344 |
| | Ar | −526.816805 | −527.049906 | −527.067698 | −527.076686 |
| | $Cl^-$ | −459.576353 | −459.803084 | −459.817303 | −459.828395 |
| 5 | $ArCl^-$ | −986.394710 | −986.873236 | −986.899972 | −986.921362 |
| | Ar | −526.817347 | −527.059275 | −527.074705 | −527.084211 |
| | $Cl^-$ | −459.576793 | −459.811568 | −459.823221 | −459.834835 |
| 6 | $ArCl^-$ | −986.394954 | | | |
| | Ar | −526.817484 | | | |
| | $Cl^-$ | −459.576903 | | | |
| 3 | $ClOO^-$ | −609.251112 | −609.904264 | −609.920659 | −609.949913 |
| | $O_2$ | −149.677187 | −150.120790 | −150.121844 | −150.141020 |
| 4 | $ClOO^-$ | −609.264251 | −609.965507 | −609.977241 | −610.009411 |
| | $O_2$ | −149.687432 | −150.160392 | −150.157885 | −150.178648 |
| 5 | $ClOO^-$ | −609.267115 | −609.988608 | | |
| | $O_2$ | −149.689875 | −150.175015 | −150.169570 | −150.190977 |
| 6 | $ClOO^-$ | −609.267489 | | | |
| | $O_2$ | −149.690143 | | | |

[a] Basis set: aug-cc-pV$n$Z on oxygen and aug-cc-pV($n$+d)Z on chlorine and argon.

[b] Core electrons excluded from the correlation treatment.

Table 3
Successive contributions to equilibrium binding energies ($D_e$, in $cm^{-1}$) for Ar–$Cl^-$ and $Cl^-$–$O_2$, corrected for BSSE[a]

| $n$[b] | HF | MP2–HF | CCSD(T)–MP2 | Total |
|---|---|---|---|---|
| $ArCl^-$ | | | | |
| 3 | 121.3 (127.1) | 329.6 (362.9) | −16.4 (−16.9) | 434.5 (473.1) |
| 4 | 124.3 (125.8) | 368.7 (387.5) | −13.5 (−16.9) | 479.5 (496.4) |
| 5 | 124.4 (124.9) | 384.7 (400.2) | −12.3 (−16.8) | 496.8 (508.4) |
| 6 | 124.3 (124.4) | | | |
| $\infty$[c] | 124.3 (124.4) | 401.5 (413.5) | −10.9 (−16.6) | 514.9 (521.3) |
| $\infty$[c,d] | 124.3 (124.4) | 401.5 (413.5) | −11.4 (−16.9) | 514.3 (521.1) |
| Expt. | | | | 523.2 ± 4.8 [29], 350 [1], 510 [1] |
| $ClOO^-$ | | | | |
| 3 | 87.4 (97.4) | 285.7 (327.0) | 71.9 (72.9) | 445.0 (497.3) |
| 4 | 96.4 (102.3) | 317.5 (343.5) | 78.5 (73.8) | 492.4 (519.6) |
| 5 | 97.2 (98.0) | 329.2 (346.6) | | |
| 6 | 97.3 (97.3) | | | |
| $\infty$[c] | 97.3 (97.3) | 341.4 (350.0) | 83.3 (74.5) | 521.9 (521.8) |
| Expt. | | | | 580 [1] |

[a] Values in parentheses are uncorrected for BSSE.
[b] Basis set: aug-cc-pV$n$Z on oxygen and aug-cc-pV($n$+d)Z on chlorine and argon.
[c] Extrapolated to the limit of a complete basis set.
[d] Coupled-cluster results for $n = 5$ excluded.

omitting them was investigated for $ArCl^-$. The effect on the computed binding energy is negligible: only $-0.6\,cm^{-1}$ (Table 3).

Three types of geometry were considered for $ClOO^-$: T-shaped ($C_{2v}$), linear ($C_{\infty v}$), and bent ($C_s$). The corresponding electronic states considered are $^3B_1, ^1A_1, ^3\Sigma^-, ^1\Delta, ^3A''$, and $^1A'$ which correlate with the dissociated limit $Cl^-$ ($^1S$) + $O_2$ ($X^3\Sigma_g^-$ or $a^1\Delta_g$). The optimized geometries obtained at the CASSCF and MCQDPT2 levels for all six states are described in Table 4. For each type of geometry, the computed triplet–singlet excitation energy is also included in Table 4. The CCSD(T) level is expected to be more reliable than CASSCF or MCQDPT2 for the ground state, since the triplet is well described by a single configuration and CCSD(T) recovers more of the dynamical correlation effects. Equilibrium geometries for the $^3B_1$, $^3\Sigma^-$, and $^3A''$ cases were therefore computed at the frozen-core CCSD(T)/aug-cc-pV(T+d)Z level; the results are included in Table 4. For the $^3A''$ case, which is most stable, the corresponding rotational constants are 1.55, 0.080, and $0.076\,cm^{-1}$. Harmonic vibrational frequencies and electric dipole absorption intensities were calculated at the CASSCF and CCSD(T) levels because analytical energy gradients were available. The results are shown in Table 5.

Binding energies for $ClOO^-$ were computed as for $ArCl^-$. Total energies are listed in Table 2 and contributions to the equilibrium binding energy are listed in Table 3. The results of basis-set extrapolations are also included in Table 3; the final result is $D_e(Cl^-–O_2) = 521.9\,cm^{-1}$. Correcting for $ZPE(O_2) = 787.2\,cm^{-1}$ and $ZPE(ClOO^-) = 831.3\,cm^{-1}$ yields $D_0(Cl^-–O_2) = 477.8\,cm^{-1}$ ($477.7\,cm^{-1}$ without the BSSE corrections). For comparison, a DFT calculation at the BLYP/aug-cc-pV(T+d)Z level, which is similar to that of [7], yields a very high value, $D_0(Cl^-–O_2) = 1995\,cm^{-1}$ ($2008\,cm^{-1}$ without BSSE corrections).

## 4. Discussion

The calculations on $ArCl^-$ were done to check the reliability of the CCSD(T) predictions. The fundamental stretching frequency in $ArCl^-$ has proved difficult to measure experimentally. In photoelectron

Table 4
Optimized (equilibrium) geometries for $ClOO^{-}$[a]

| | $r$(Cl–O) (pm) | $r$(Cl–O′) (pm) | $r$(O–O′) (pm) | $\theta$(Cl–O–O′) (°) | $E + 609$ (Hartree) | $T_e$ (cm$^{-1}$)[b] |
|---|---|---|---|---|---|---|
| CASSCF(8, 6) | | | | | | |
| $^3B_1$ | 404.2 | 404.2 | 121.5 | 81.4 | −0.329988 | 0 |
| $^1A_1$ | 381.5 | 381.5 | 122.8 | 80.7 | −0.298103 | 6998 |
| $^3\Sigma^-$ | 390.4 | 512.3 | 121.8 | 180 | −0.329744 | 0 |
| $^1\Delta$ | 400.1 | 523.2 | 123.1 | 180 | −0.297027 | 7181 |
| $^3A''$ | 403.3 | 406.7 | 121.5 | 83.0 | −0.329988 | 0 |
| $^1A'$ | 380.7 | 381.6 | 122.8 | 81.1 | −0.298103 | 6998 |
| MCQDPT2(8, 6) | | | | | | |
| $^3B_1$ | 402.3 | 402.3 | 121.8 | 81.3 | −0.923552 | 0 |
| $^1A_1$ | 403.7 | 403.7 | 122.7 | 81.3 | −0.885324 | 8390 |
| $^3\Sigma^-$ | 341.1 | 463.6 | 122.5 | 180 | −0.923804 | 0 |
| $^1\Delta$ | 340.2 | 463.6 | 123.4 | 180 | −0.886832 | 8114 |
| $^3A''$ | 358.2 | 366.8 | 122.0 | 84.3 | −0.923866 | 0 |
| $^1A'$ | 346.8 | 470.3 | 123.4 | 179.2 | −0.886842 | 8126 |
| CCSD(T) | | | | | | |
| $^3B_1$ | 356.9 | 356.9 | 121.2 | 80.2 | −0.949909 | |
| $^3\Sigma^-$ | 341.0 | 462.7 | 121.7 | 180 | −0.949782 | |
| $^3A''$ | 343.2 | 375.6 | 121.2 | 96.0 | −0.949913 | |
| BLYP/DZP++ [7] | | | | | | |
| $^3A''$ | 310.7 | 402 | 127.2 | 128.2 | | 0 |
| $^1A'$ | 243.6 | 324 | 129.1 | 117.7 | | 7300 |

[a] aug-cc-pV(T+d)Z basis set on chorine and aug-cc-pVTZ basis set on oxygen.

[b] Excitation energy to singlet state for given point group ($C_{2v}$, $C_{\infty v}$, or $C_s$).

Table 5
Harmonic vibrational frequencies and absorption intensities for $ClOO^{-}$[a,b]

| | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) | $I_1$ (km mol$^{-1}$) | $I_2$ (km mol$^{-1}$) | $I_3$ (km mol$^{-1}$) |
|---|---|---|---|---|---|---|
| CASSCF(8, 6) | | | | | | |
| $^3B_1$ | 1549 | 32 | 40 | 0.02 | 14.3 | 0.06 |
| $^1A_1$ | 1453 | 47 | 51 | 0.12 | 14.6 | 0.02 |
| $^3\Sigma^-$ | 1534 | 32 | 14 | 3.70 | 15.2 | 0.26 |
| $^1\Delta$ | 1443 | 25 | $52i$ | 1.96 | 14.8 | 0.09 |
| $^3A''$ | 1548 | 33 | 29 | 0.02 | 14.3 | 3.58 |
| $^1A'$ | 1453 | 46 | 45 | 0.12 | 13.0 | 1.76 |
| CCSD(T) | | | | | | |
| $^3B_1$ | 1580 | 56 | $11i$ | 0.22 | 14.5 | 0.001 |
| $^3\Sigma^-$ | 1547 | 55 | 10 | 11.0 | 16.1 | 1.52 |
| $^3A''$ | 1591 | 58 | 14 | 0.96 | 15.5 | 0.21 |
| BLYP/DZP2++ [7] | | | | | | |
| $^3A''$ | 1339 | 119 | 52 | | | |
| Expt. | | 46.8 [1][c] | | | | |

[a] aug-cc-pV(T+d)Z basis set on chlorine and aug-cc-pVTZ basis set on oxygen.

[b] The antisymmetric vibrational frequency is labeled $\omega_3$.

[c] Presumed here to be the Cl–O stretching frequency, $\omega_2$.

studies, the fundamental frequency, $v''(1\text{–}0)$, of the anion (lower state) is determined as the difference between pairs of $v' \leftarrow 0$ and $v' \leftarrow 1$ peaks. The second study [1] did not identify any such pairs, but the first study [29] showed three, yielding the alternative values for the fundamental $v''(1\text{–}0) = 53.0$, 46.8, or 52.5 $\text{cm}^{-1}$. Both studies identified a pair of peaks (1–0 and 1–3) that allow $v''(3\text{–}0) = 148.0\,\text{cm}^{-1}$ [29] or 139.0 $\text{cm}^{-1}$ [1] to be inferred. Other pairs of peaks can provide values for the $v''(3\text{–}2)$ and $v''(2\text{–}1)$ intervals. Subtraction yields indirect values of $v''(1\text{–}0)$ ranging from 50 to 57 $\text{cm}^{-1}$. Finally, the study by Lenzer et al. included a careful spectral simulation that yielded the estimate $v''(1\text{–}0) = 53.09\,\text{cm}^{-1}$ [29]. The measurement challenges notwithstanding, the reported experimental estimates are 53 $\text{cm}^{-1}$ [29] and 53.4 $\text{cm}^{-1}$ [1]. The harmonic value calculated here, 52 $\text{cm}^{-1}$, agrees with these estimates.

Likewise, there are no direct experimental measurements of the bond length or binding energy in $\text{ArCl}^-$. However, the aforementioned spectral simulation provided the experimental estimates $r_e(\text{Ar–Cl}^-) = 378 \pm 8\,\text{pm}$ and $D_0(\text{Ar–Cl}^-) = 494.0 \pm 4.8\,\text{cm}^{-1}$ [29]. Both results agree with the present, calculated values of 372 pm and 489 $\text{cm}^{-1}$, respectively. Earlier calculations provided values of $r_e$ within 3 pm of the present calculations but dissociation energies smaller by 38 $\text{cm}^{-1}$ [30] and 14 $\text{cm}^{-1}$ [31]. Thus, the tests on $\text{ArCl}^-$ are encouraging. Alternative experimental values for $D_0(\text{Ar–Cl}^-)$ of 350 and 510 $\text{cm}^{-1}$ are available [1]. The lower value was obtained by Birge–Sponer extrapolation for the anion and the higher value was from Birge–Sponer extrapolation for neutral ArCl combined with a thermodynamic cycle involving electron affinities. Birge–Sponer extrapolation can provide only a crude estimate of the dissociation energy [32], especially when based upon such limited and approximate data, so these values are not useful for benchmarking purposes.

For comparison purposes, DFT calculations were also done for the structure and binding energy of $\text{ArCl}^-$. At the BLYP/aug-cc-pV(T+d)Z level, $r_e(\text{Ar–Cl}^-) = 401\,\text{pm}$, $\omega_e = 37\,\text{cm}^{-1}$, and $D_0(\text{Ar–Cl}^-) = 183\,\text{cm}^{-1}$ (189 $\text{cm}^{-1}$ without correcting for BSSE). Thus, this functional provides the correct qualitative description, as a weakly bound complex, but does not provide quantitative accuracy.

The performance of the multireference calculations was tested on the $O_2$ molecule. The principal quantity of interest is the singlet excitation energy. As shown in Table 1, the MCQDPT2 value of $T_e(\text{a}^1\Delta_g) = 8149\,\text{cm}^{-1}$ is in error by only 231 $\text{cm}^{-1}$. Thus, these test calculations indicate that the MCQDPT2 procedure is reliable here.

For $\text{ClOO}^-$, a triplet ground state is expected for a weak complex of $\text{Cl}^-$ and $O_2$, whereas a singlet ground state is expected for a covalently bonded chloroperoxide anion. The multireference calculations show that the ground state is a spin triplet, with the singlet state higher by approximately the same interval (about 23 $\text{cm}^{-1}$ less) as in the free $O_2$ molecule (Table 4). Thus, $T_e(\tilde{\text{a}}^1\text{A}')$ is estimated to be 7895 $\text{cm}^{-1}$ in $\text{ClOO}^-$. The calculated equilibrium geometry is sensitive to the treatment of electron correlation. At the CASSCF level, the lowest triplet and singlet are both T-shaped ($C_{2v}$ point group), with linear geometries higher by 54 and 236 $\text{cm}^{-1}$, respectively. When dynamical correlation is included at the MCQDPT2 level, the triplet is a slightly asymmetric side-on complex ($C_s$ point group) and the singlet is nearly linear, with the corresponding linear triplet and T-shaped singlet geometries higher by 69 and 333 $\text{cm}^{-1}$, respectively. The triplet can be characterized more accurately at the CCSD(T) level, which predicts a distorted side-bound geometry ($C_s$ point group). However, the T-shaped saddle point and linear minimum lie only 0.7 and 29 $\text{cm}^{-1}$ higher, respectively. Thus, the bending potential is very soft, as expected for a weakly bound complex.

The frequency of the O–O stretching vibration and the equilibrium O–O distance in $\text{ClOO}^-$ are close to the corresponding values in free $O_2$ (Tables 4 and 5). The bending potential ($v_3$, using the numbering of Table 5) is probably quite anharmonic, but its harmonic frequency is predicted to be 14 $\text{cm}^{-1}$. This indicates that the bending ZPE (ca. 7 $\text{cm}^{-1}$) exceeds the energy required to access the $C_{2v}$ saddle point (0.7 $\text{cm}^{-1}$), and that the symmetry of the vibrational ground-state wavefunction ($v_3 = 0$) is therefore $C_{2v}$, for a ground-state electronic designation of $\tilde{X}^3B_1$. Since the linear minimum (29 cm$^{-1}$) lies above the $v_3 = 0$ level (ca. 7 cm$^{-1}$), the $O_2$ fragment is not free to rotate in the vibrational ground state.

The harmonic frequency of the $Cl^-$–$O_2$ stretching vibration ($v_2$) is calculated to be 58 cm$^{-1}$ (Table 5), which is higher than the experimental value of 46.8 cm$^{-1}$ [1]. However, examining the tabulated experimental data in [1] reveals greater uncertainties than are suggested by this precise value. The anion fundamental frequency $v''(1\text{–}0)$ can be inferred from pairs of peaks $v' \leftarrow 0$ and $v' \leftarrow 1$, as previously for $ArCl^-$. Two such pairs are available, for $v' = 0$ and $v' = 1$, yielding anion fundamentals of 53.5 and 46.8 cm$^{-1}$, respectively. Peaks are assigned with $v''$ as high as 4, apparently corresponding to an internal energy of 180 cm$^{-1}$ [1]. The lowest-frequency vibration is the bend (i.e., the frustrated internal rotation), which will also be excited, and some of the peaks must correspond to transitions involving this vibration. Finally, the peak that lies 113.4 cm$^{-1}$ to the red of the strong peak is labeled 2–1 in Fig. 7 and labeled 1–2 in Table 6 of [1]; both choices are inconsistent with the other assignments. Further work is needed to assign the vibrational structure convincingly.

A third band, lying 506 cm$^{-1}$ above the lowest, was assigned to the fundamental bending vibration in neutral ClOO. However, the corresponding value in cryogenic matrices has been measured as 408.3 cm$^{-1}$ (Ar) and 413.7 cm$^{-1}$ (Ne) [33]. In the gas phase, the bending fundamental has been predicted at 391 cm$^{-1}$ by using high-level ab initio calculations [34]. Thus, an alternative assignment for this photoelectron band appears necessary.

No experimental geometry is available for neutral ClOO ($\tilde{X}^2A''$). An early cryogenic study is sometimes cited, but that geometry was an estimate based upon a force field analysis and with the lowest vibrational frequency almost twice too high [35]. Likewise, the more definitive study by Müller and Willner [36] simply adopted a theoretical geometry [34] after finding it consistent with spectroscopic observations.

The most reliable theoretical study yielded $r(\text{Cl–O}) = 213.9$ pm, $r(\text{O–O}') = 120.1$ pm, and $\theta(\text{Cl–O–O}') = 115.7^\circ$, from multireference configuration interaction (MRCI) calculations [34]. The principal difference from the anion geometry is that $r(\text{Cl–O}) = 343$ pm in $ClOO^-$, although the equilibrium bond angle also closes to 96° (Table 4). That is, the Cl–O distance decreases by about 129 pm (38%) upon photodetachment. A qualitatively similar result has been obtained from DFT calculations both for ClOO [7] and for the analogous BrOO system [37]. Such a large contraction is expected to lead to an extensive vibrational progession in $v_2$, the soft symmetric stretch. In contrast, the bond lengths in $ArCl^-$ and in ArCl differ by only 2 or 3 pm [29,31], leading one to expect a sharp peak in the photoelectron spectrum of $ArCl^-$. The experimental photoelectron spectrum for $ArCl^-$ is as expected [1,29]. However, the spectrum for $ClOO^-$ is a surprise, showing a weak vibrational progression instead of a strong one, and characterized by $v_2' = 24.5$ cm$^{-1}$ [1], far smaller than the theoretical prediction of 181 cm$^{-1}$ [34] and the matrix-isolation values, which lie between 192 and 203 cm$^{-1}$ for three different matrices [33]. Consequently, Distelrath and Boesl speculated that the photoelectron experiment accesses a van der Waals isomer of neutral ClOO, not the ground state [1]. If so, as is likely, then the reported electron affinity is too high by an amount equal to the isomerization energy.

Theoretical studies of neutral ClOO have not considered Cl–O distances as large as found here for the anion (ca. 343 pm). Thus, a van der Waals isomer of ClOO appears not to have been considered computationally. The best calculations [34] only probed distances up to 254 pm. Earlier multireference calculations explored up to about 318 pm, but using configuration selection thresholds, which cause small distortions in the potential surface [38]. Single-reference methods [39–41] would probably be inappropriate for a low-spin-coupled van der Waals complex between Cl and $O_2$ (a tri-radical system). Contemporary DFT approaches [41,42] fail to describe dispersion interactions [8–10] and are therefore inappropriate for van der Waals complexes. An ab initio search for a van der Waals isomer is underway.

Electron detachment from the triplet ground state of $ClOO^-$ can produce both doublet and quartet states of neutral ClOO. The ground state of ClOO is $\tilde{X}^2A''$; the low-lying $\tilde{A}^2A'$ state is repulsive [38]. The quartet states $\tilde{a}^4A''$ and $\tilde{b}^4A'$ are also repulsive [7]. At large Cl–O distances, the low-lying states of ClOO will be nearly degenerate [38]. Indeed, a calculation of vertical detachment energies [state-averaged MCQDPT2(13,9)/aug-cc-pV(T+d)Z] predicts that all four neutral states will lie within a range of about $200\,cm^{-1}$. Thus, the photoelectron experiment is expected to produce a superposition of spectra from four closely-spaced, final electronic states, complicating the spectral interpretation. Bound states with the best Franck–Condon overlap with the anion will be most prominent, since their intensity will be concentrated in a few peaks.

The binding energy $D_0(Cl^-–O_2)$ is calculated to be $478\,cm^{-1}$ ($5.72\,kJ\,mol^{-1}$). This is significantly lower than the experimental estimate of $560\,cm^{-1}$ derived from a Birge–Sponer extrapolation. However, since the experimental vibrational assignments are problematic, Birge–Sponer extrapolation is even more unreliable than usual (see Section 4 for $ArCl^-$). Thus, the present computational result is the most reliable value available. As discussed above, the binding energy computed for $ArCl^-$ is too low by $5 \pm 5\,cm^{-1}$ compared with the best experimental estimate. For $ArCl^-$ there is also a discrepancy of $7\,cm^{-1}$ between the results with and without corrections for BSSE. In contrast, the result for $ClOO^-$ is independent of any corrections for BSSE, suggesting that it is more fully converged than the result for $ArCl^-$. This is expected, since the triatomic molecule has more basis functions for the same nominal basis set. The uncertainty (type B uncertainty, 90% confidence) in the calculated binding energy of $ClOO^-$ is estimated to be $10\,cm^{-1}$. Given $\Delta_f H_0^\circ(Cl^-) = -229.08 \pm 0.20\,kJ\,mol^{-1}$ [43], this implies a standard, gas phase enthalpy of formation $\Delta_f H_0^\circ(ClOO^-) = -234.80 \pm 0.23\,kJ\,mol^{-1}$.

A simple thermodynamic cycle can be used to derive the binding energy $D_0(Cl–O_2)$ for the van der Waals isomer of neutral ClOO [1]. It is given by Eq. (3). When experimental electron affinities and the present, theoretical anionic binding energy are adopted, the result is $D_0(Cl–O_2;\ \text{van der Waals}) = 97 \pm 10\,cm^{-1}$ ($1.2 \pm 0.1\,kJ\,mol^{-1}$).

$$D_0(Cl–O_2) = D_0(Cl^-–O_2) + EA(Cl) - EA(ClOO) \tag{3}$$

## 5. Conclusions

The present calculations support the conclusion, by Distelrath and Boesl, that $ClOO^-$ is a weakly bound complex and not a chloroperoxide ion. However, the calculations also predict a major change in geometry upon photodetachment. Consequently, the ground state of neutral ClOO is expected to be manifested in the photoelectron spectrum as a very long vibrational progression. Since the band intensity is spread over many closely-spaced peaks, all are weak and probably not observed in the experimental spectrum. The observed spectrum probably derives from a van der Waals isomer or excited state of ClOO, as suggested by Distelrath and Boesl. Vibrational structure, however, is difficult to assign. The binding energy of $Cl^-$ to $O_2$ is about 3% less than that to Ar.

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## References

[1] V. Distelrath, U. Boesl, Faraday Discuss. 115 (2000) 161.
[2] U. Berzinsh, M. Gustafsson, D. Hanstorp, A. Klinkmuller, U. Ljungblad, A.M. Martenssonpendrill, Phys. Rev. A 51 (1995) 231.
[3] C.E. Moore, Atomic Energy Levels, US Govt. Printing Office, Washington, DC, 1971.
[4] J.M. Nicovich, K.D. Kreutter, C.J. Shackelford, P.H. Wine, Chem. Phys. Lett. 179 (1991) 367.
[5] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, J. Troe, J. Chem. Phys. 95 (1991) 6463.

[6] R.L. Mauldin III, J.B. Burkholder, A.R. Ravishankara, J. Phys. Chem. 96 (1992) 2582.

[7] Q.-S. Li, S.-F. Lü, W.-G. Xu, Y. Xie, H.F. Schaefer III, J. Phys. Chem. A 106 (2002) 12324.

[8] S. Kristyán, P. Pulay, Chem. Phys. Lett. 229 (1994) 175.

[9] J.M. Pérez-Jordá, A.D. Becke, Chem. Phys. Lett. 233 (1995) 134.

[10] Q. Wu, W. Yang, J. Chem. Phys. 116 (2002) 515.

[11] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.

[12] R.A. Kendall, T.H. Dunning Jr., J. Chem. Phys. 96 (1992) 6796.

[13] T.H. Dunning Jr., K.A. Peterson, A.K. Wilson, J. Chem. Phys. 114 (2001) 9244.

[14] D. Feller, K. Schuchardt, Extensible Computational Chemistry Environment Basis Set Database. Developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest National Laboratory. http://www.emsl.pnl.gov:2080/forms/basisform.html.

[15] H. Nakano, J. Chem. Phys. 99 (1993) 7983.

[16] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.

[17] A.A. Granovsky, PC-GAMESS, version 6.0, Moscow State University, Moscow, 2000.

[18] ACES II, release 3.0, is a program product of the Quantum Theory Project, University of Florida. Authors: J.F. Stanton, J. Gauss, J.D. Watts, M. Nooijen, N. Oliphant, S.A. Perera, P.G. Szalay, W.J. Lauderdale, S.A. Kucharski, S.R. Gwaltney, S. Beck, A. Balková, D.E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Hober, R.J. Bartlett. Integral packages included are VMOL (J. Almlöf, P.R. Taylor); VPROPS (P. Taylor); ABACUS (T. Helgaker, H.J.A. Jensen, P. Jørgensen, J. Olsen, P.R. Taylor).

[19] G.G. Balint-Kurti, P. Pulay, J. Mol. Struct. 341 (1995) 1.

[20] R.D. Johnson III, FGH1D, version 1.01, National Institute of Standards and Technology, Gaithersburg, MD, 1998.

[21] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, Chem. Rev. 94 (1994) 1873.

[22] B. Fernández, H. Koch, J. Chem. Phys. 109 (1998) 10255.

[23] T. van Mourik, A.K. Wilson, K.A. Peterson, D.E. Woon, T.H. Dunning Jr., Adv. Quant. Chem. 31 (1998) 105.

[24] T. van Mourik, A.K. Wilson, T.H. Dunning Jr., Mol. Phys. 96 (1999) 529.

[25] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, J. Olsen, Chem. Phys. Lett. 302 (1999) 437.

[26] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Chem. Phys. Lett. 286 (1998) 243.

[27] J.M.L. Martin, G. de Oliveira, J. Chem. Phys. 111 (1999) 1843.

[28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, version Gaussian Inc., Pittsburgh, PA, 1998.

[29] T. Lenzer, I. Yourshaw, M.R. Furlanetto, G. Reiser, D.M. Neumark, J. Chem. Phys. 110 (1999) 9578.

[30] F.Y. Naumkin, F.R.W. McCourt, Chem. Phys. Lett. 292 (1998) 63.

[31] A.A. Buchachenko, R.V. Krems, M.M. Szczesniak, Y.-D. Xiao, L.A. Viehland, G. Chalasinski, J. Chem. Phys. 114 (2001) 9919.

[32] G. Herzberg, Spectra of Diatomic Molecules, vol. 1, 2nd ed., Van Nostrand Reinhold, New York, 1950.

[33] Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules, in: M.E. Jacox (Ed.), NIST Chemistry WebBook, National Institute of Standards and Technology, Gaithersburg, MD, 2001; http://webbook.nist.gov.

[34] K.A. Peterson, H.-J. Werner, J. Chem. Phys. 96 (1992) 8948.

[35] A. Arkell, I. Schwager, J. Am. Chem. Soc. 89 (1967) 5999.

[36] H.S.P. Müller, H. Willner, J. Phys. Chem. 97 (1993) 10589.

[37] Y. Xie, H.F. Schaefer III, Y. Wang, X.-Y. Fu, R.-Z. Liu, Mol. Phys. 98 (2000) 879.

[38] J.A. Jafri, B.H. Lengsfield III, C.W. Bauschlicher Jr., D.H. Phillips, J. Chem. Phys. 83 (1985) 1693.

[39] J.S. Francisco, S.P. Sander, J. Chem. Phys. 99 (1993) 6219.

[40] V.R. Morris, S.C. Bhatia, T.S. Dibble, J.S. Francisco, J. Chem. Phys. 104 (1996) 5345.

[41] M. Alcami, O. Mó, M. Yáñez, I.L. Cooper, J. Chem. Phys. 112 (2000) 6131.

[42] A. Beltrán, J. Andrés, S. Noury, B. Silvi, J. Phys. Chem. A 103 (1999) 3078.

[43] L.V. Gurvich, I.V. Veyts, C.B. Alcock (Eds.), Thermodynamic Properties of Individual Substances, Hemisphere, New York, 1989.

[44] Constants of Diatomic Molecules (data prepared by J.W. Gallagher, R.D. Johnson III), in: K.P. Huber, G. Herzberg (Eds.), NIST Chemistry WebBook, National Institute of Standards and Technology, Gaithersburg, MD, 2001; http://webbook.nist.gov.

[45] L. Herzberg, G. Herzberg, Astrophys. J. 105 (1947) 353.