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Microsolvation of the chlorine oxide anion and chlorine oxide radical: Structures and energetics of the $ClO^- \cdot (H_2O)_n$ and $ClO \cdot (H_2O)_n$ $n = 1$–4 clusters

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Abstract

Counterpoise corrected geometries, absolute energies, and vertical detachment energies of the $ClO^- \cdot (H_2O)_n$ $n = 1$–4 clusters were determined for the first time using high-level ab initio [up to CCSD(T)] and density functional theory calculations. For the $n > 1$ clusters, a number of low-energy, isomeric structures are obtained. The global minima structures are characterized by water hydrogen bonds to the oxygen of ClO^-, with the Cl protruding from the cluster surface. By contrast, the neutral $ClO \cdot (H_2O)_n$ $n = 1$–4 cluster structures are controlled by water–water interactions, with ClO being only weakly bound. Implications for the atmospheric chemistry and photodetachment spectroscopy of these species are briefly discussed.

1. Introduction

The important role played by halogen oxides such as ClO in the catalytic destruction of ozone in the Earth's stratosphere is well acknowledged [1]. At higher altitudes in the D region, the negatively charged analogue, ClO^-, also occurs [2]. Although present in low mesospheric concentrations, ClO^- is highly reactive and involved in reactions with important species such as O, NO, and NO_2[2]. Over recent years, the role played by small hydrated clusters within atmospheric chemistry cycles has been increasingly recognized [3–5]. For example, the $ClO \cdot H_2O$ radical–molecule complex has been suggested [3] to enhance the formation of the ClO dimer through:

$$ClO \cdot H_2O + ClO \rightarrow Cl_2O_2 + H_2O \qquad (1)$$

This work aims to explore the structures and energetics of the $ClO^- \cdot (H_2O)_n$ $n = 1$–4 micro-solvated clusters using computational chemistry. The bare ClO^- ion has been studied experimentally using anion photodetachment spectroscopy [6,7], with several theoretical studies complementing these measurements [8,9]. However, our work is the first to explore the microsolvation of ClO^-, and therefore investigate the influence of hydration on the atmospheric properties of the ion. Such studies also provide insight into the likely properties of ionic aerosols. The neutral $ClO \cdot H_2O$ complex has been widely studied due to its importance in the stratosphere [3,10,11], and therefore provides a valuable comparison to the anionic analogue. We build on the earlier $ClO \cdot H_2O$ work by also exploring structures of the neutral $ClO \cdot (H_2O)_n$ $n = 2$–4 clusters, thus allowing us to assess the feasibility of studying both the anionic and neutral systems using anion photodetachment techniques [12,13].

2. Computational methods

All calculations [B3LYP and MP2(frozen core)] were performed using GAUSSIAN 03, [14] with standard basis sets. For the DFT calculations, the B3LYP functional was selected since it provides reasonable geometric structures

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and electron affinities for a range of negative ions and their hydrated clusters [15–17]. The automated counterpoise (CP) correction procedure of Dannenberg [18] was employed for all geometry optimizations to remove any anomalous effects of BSSE on the cluster structures. High-level [CCSD and CCSD(T)] single point calculations were also performed to test the relative cluster energies obtained.

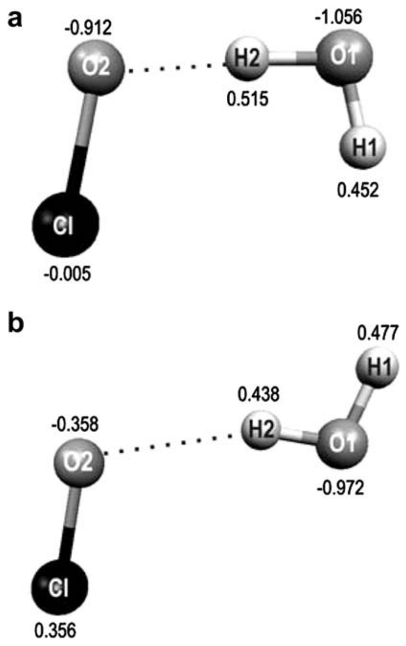

Fig. 1. Geometric structures (MP2/aug-cc-pVDZ), atom labels, and NPA atomic partial charges of the CP-corrected minima of: (a) $ClO^- \cdot H_2O$; and (b) $ClO \cdot H_2O$.

Harmonic vibrational frequencies were calculated to confirm that clusters corresponded to local minima. All open shell species are essentially free of spin contamination ($\langle S^2 \rangle$ values below 0.77). Vertical detachment energies (VDE) were calculated as described previously [16]. Zero-point energy (ZPE) corrected values are included where stated. NPA partial charges are derived from HF densities. Detailed geometric parameters for the $n = 2$–4 clusters are not presented in this brief letter, but are available (with vibrational frequencies) on request.

3. Results and discussion

3.1. The $ClO^- \cdot H_2O$ and $ClO \cdot H_2O$ clusters

Fig. 1a presents the planar C_s symmetry global minimum structure of $ClO^- \cdot H_2O$. The structure displays a primary water hydrogen-bond (H2–O2) to the oxygen of ClO^-, with a secondary hydrogen bond (H1–Cl) to the Cl of the ion. Geometric parameters and binding energies are listed in Table 1. Comparing the $ClO^- \cdot H_2O$ cluster geometry with the uncomplexed monomers illustrates that the R_{H1O1} bond length is slightly shorter in the complex, while the R_{O1H2} bond is significantly elongated. (At the B3LYP/aug-cc-pVDZ level, r_{H_2O} is 0.965 Å, $\theta_{H_2O} = 104.8°$, and $r_{ClO^-} = 1.741$). This phenomenon is well known in hydrated anion clusters, and can be attributed to ion-to-solvent charge transfer [19].

Fig. 1b displays the near-planar C_1 symmetry neutral $ClO \cdot H_2O$ cluster structure which represents the only neutral minimum obtained in this study. In contrast to the anionic cluster, $ClO \cdot H_2O$ contains only a single water

Table 1
Geometric parameters,[a] and cluster binding energies (in eV),[b] for the global minima of the $ClO^- \cdot H_2O$ and $ClO \cdot H_2O$ clusters

	MP2/6-311++G**	MP2/aug-cc-pVDZ	B3LYP/aug-cc-pVDZ	B3LYP/aug-cc-pVTZ	B3LYP/aug-cc-pVQZ
$ClO^- \cdot H_2O$					
R_{H1O1}	0.959	0.965	0.963	0.960	0.959
R_{O1H2}	1.008	1.021	1.024	1.021	1.020
R_{H2O2}	1.662	1.629	1.604	1.602	1.604
R_{O2Cl}	1.705	1.711	1.735	1.703	1.694
R_{H1Cl}	3.316	3.258	3.351	3.359	3.356
A_{H1O1H2}	100.6	101.2	102.4	102.7	102.7
A_{O1H2O2}	174.7	176.7	178.6	178.3	178.1
A_{H2O2Cl}	107.4	103.6	105.6	106.6	106.8
Binding energy	0.964 (0.835)	0.925 (0.853)	0.863 (0.798)	0.848 (0.784)	0.845 (0.780)
$ClO \cdot H_2O$					
R_{H1O1}	0.959	0.964	0.964	0.961	0.960
R_{O1H2}	0.962	0.969	0.969	0.966	0.965
R_{H2O2}	2.092	2.098	2.096	2.101	2.092
R_{O2Cl}	1.590	1.617	1.617	1.588	1.580
A_{H1O1H2}	103.9	105.0	105.0	105.3	105.4
A_{O1H2O2}	159.0	169.2	169.9	168.8	168.0
A_{H2O2Cl}	110.8	109.5	110.1	112.4	112.2
Binding energy	0.136 (0.093)	0.133 (0.101)	0.099 (0.054)	0.100 (0.055)	0.107 (0.052)

[a] Distances are in Å, and angles in °.

[b] ZPE corrected binding energies are included in parentheses.