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He I Photoelectron Spectroscopic (PES) Study on the Electron Structure of Perchloric Acid, $HOClO_3$, and Fluorine Perchlorate, $FOClO_3$

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The He I photoelectron spectra (PES) of $HOClO_3$ and $FOClO_3$ are reported. The assignments of the PES bands are made on the basis of band shapes, relative band intensities, and the results of ab initio calculations using GAUSSIAN 94 at the 6-31G* basis set level. The two peaks (at 12.37 and 12.77 eV) in the first PES band of $HOClO_3$ are designated as electron ionizations from HOMO 8a″(25), SHOMO 7a″(24), and 17a′(23) orbitals, respectively, and they can be attributed to a Jahn−Teller effect on the largely lone-pair orbitals of three oxygen atoms in the ClO_3 atomic group of $HOClO_3$. The absence of splitting in the first PES band of $FOClO_3$ centered near 13.20 eV is attributed to a loss of C_{3v} symmetry in the ClO_3 atomic group of $FOClO_3$. This band is assigned to electron ionizations of the HOMO 9a″(29), SHOMO 8a″(28), and 20a′(27) orbitals, in which the three oxygen atoms of the ClO_3 atomic group of the $FOClO_3$ molecule hold dominant weight.

Introduction

It is well-known that halogen atoms released in the stratosphere by solar UV photolysis of halogenated compounds can remove ozone via the production of XO, where X is F, Cl, Br, or I, in the catalytic chain (reactions 1 and 2)

$$X+O_3 \rightarrow XO+O_2 \qquad (1)$$

$$XO+O \rightarrow X+O_2 \qquad (2)$$

The halogenated nitrates $XONO_2$, which can form in the stratosphere by the reaction of XO with NO_2, can be an important temporary reservoir of halogen atoms. They are also involved in the chemical reactions on the surface of polar stratospheric clouds (PSCs), which lead to ozone depletion.[1−5]

Recently, systematic He I photoelectron spectroscopic (PES) studies on the electronic structures of $XONO_2$, where X is F, Cl, or Br, were carried out in this laboratory.[6−8] As part of our systematic work on the chemical species involved in ozone depletion, He I PES studies on the electronic structure of $XOClO_3$, where X is H, F, Cl, or Br, are also being pursued, as these also play an important role as novel temporary reservoir species in stratospheric chemistry, including ozone depletion.[9] We now report PES studies on the electronic structure of both $HOClO_3$ and $FOClO_3$ for the first time. In order to assign the PES bands, ab initio Gaussian 94 SCF MO calculations using 6-31G* atomic basis sets have also been performed for both molecules.

Experimental Section

Caution! Although no explosions occurred during the present study, both $FOClO_3$ and $HOClO_3$ are highly sensitive and powerful explosives. They are particularly dangerous in the presence of organic or oxidizable materials, and they should be handled only in small quantities and with appropriate safety precautions.

1. Preparations of $FOClO_3$ and $HOClO_3$. $FOClO_3$ was synthesized according to the literature method[10,11] by the direct fluorination of $HClO_4$. Fluorine diluted with helium was passed through 72% perchloric acid, which was held at 55 °C; the products were condensed at liquid nitrogen (−196 °C) and then purified by fractional condensation as verified by IR spectroscopy.

$HOClO_3$ was prepared by the literature method[12] from 72% perchloric acid and fuming sulfuric acid, mixed in the proportions 1 to 4. The mixture ranged in temperature from 30 to 65 °C, and the crude product was fractionated through a series of traps at −20, −90, and −196 °C. Pure $HOClO_3$ was obtained in the middle fraction.

2. PES Measurement. The He I (21.22 eV) photoelectron spectra of both $FOClO_3$ and $HOClO_3$ have been measured on the double-chamber UPS machine-II built specifically to detect transient species.[13] The operational resolution for the $^2P_{3/2}$ peak of argon (Ar^+) is around 25 meV. Experimental ionization potentials (IPs) were calibrated by simultaneous addition of small amounts of argon and methyl iodide to the sample. Digitized spectra, time-averaged for periods of around 40 min, are also obtained.

In order to assign the PES bands, the Hartree−Fock (HF) SCF MO calculations at the 6-31G* basis set levels are performed, using the program package Gaussian 94[14] on a Sun Ultra Workstation. The geometries of both $HOClO_3$ and $FOClO_3$ are taken from the results of fully optimized Hartree−Fock (HF) calculations at the 6-31G* level.

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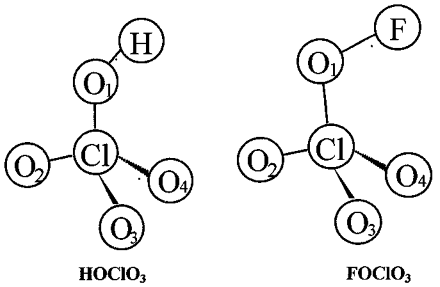


Figure 1. Geometric structures optimized by ab initio calculation using GAUSSIAN 94 at the 6-31G* basis set level for both $FOClO_3$ and $HOClO_3$.

TABLE 1: Minimum-Energy Geometries[a] Optimized Using ab Initio Calculation at the 6-31G* Basis Set Level for Both $HOClO_3$ and $FOClO_3$

coordinate	$HOClO_3$	$FOClO_3$
XO_1[b]	0.9551	1.3587
O_1Cl	1.5971	1.6611
ClO_2	1.4068	1.4057
ClO_3	1.4161	1.4063
ClO_4	1.4161	1.4063
XO_1Cl	108.01	105.71
O_1ClO_2	102.24	98.31
O_1ClO_3	105.10	105.03
O_1ClO_4	105.10	105.03
O_2ClO_4	114.80	115.62
O_2ClO_3	114.80	115.62
O_3ClO_4	113.10	114.50

[a] The bond length unit is angstroms; the bond angle unit is degrees. [b] XO_1: For $HOClO_3$ X means H; for $FOClO_3$ X means F.

Results and Discussion

1. The Minimum-Energy Geometries for $HOClO_3$ and $FOClO_3$. The minimum-energy geometries, as obtained above for both $HOClO_3$ and $FOClO_3$ molecules, are shown in Figure 1.

Table 1 gives the parameters of the minimum-energy optimized geometries for both $HOClO_3$ and $FOClO_3$ molecules.

From Table 1, it is seen that the ClO_3 atomic group basically preserves a C_{3v} symmetry, which is consistent with the result of reported literature[15] for the $HOClO_3$ molecule. However, in the $FOClO_3$ molecule, the C_{3v} symmetry of the ClO_3 atomic group is distorted. This can be attributed to the large electronegativity of the fluorine atom.

2. Assignment of PES Bands for $HOClO_3$ and $FOClO_3$. The PE spectra of both $FOClO_3$ and $HOClO_3$ are given in Figure 2.

It is seen that three bands with very high intensity in the lower ionization potential region (<16.50 eV) appear in the PE spectra of the two molecules, implying that the photoionization cross section of the corresponding molecular orbitals is large for He I radiation. This is a characteristic of MOs in which the light elements hold dominant weights.

The first band with low ionization potentials (at 12.37 and 12.77 eV) in the PE spectrum of $HOClO_3$ is attributed to ionization of oxygen lone pairs in the ClO_3 group. The combination of lone-pair orbitals for the three oxygen atoms of ClO_3, assuming a C_{3v} symmetry, transforms as $a_1 + e$ representations. A direct overlap can be expected to stabilize the a_1 orbitals relative to the e orbitals. Simple overlap considerations also suggest that through-bond interaction should also place e above a_1. That is to say, the lowest IP peak (at 12.37 eV) should have approximately twice the area of the next peak (12.77 eV). However, the area of the first PES peak (12.37 eV) in $HOClO_3$ is observed to be half of the next peak (12.77 eV). This fact can be explained by a through-space interaction of the three lone-pair orbitals of the oxygen atoms in the ClO_3 atomic group of $HOClO_3$, the e level being above a_1, combined with Jahn–Teller removal of the degeneracy of the ^2E state.

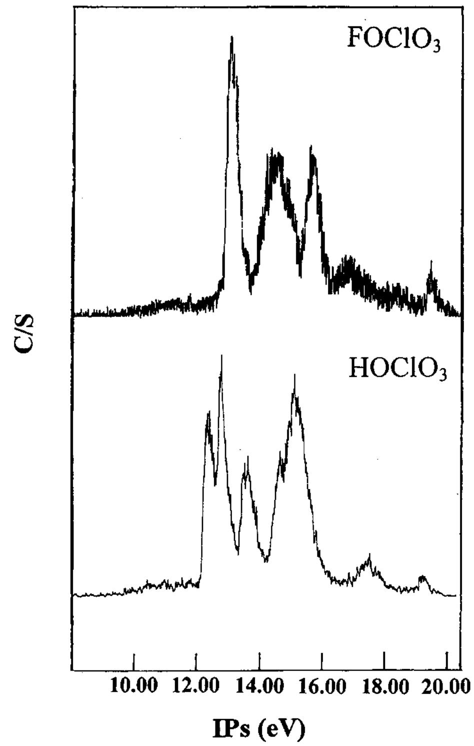
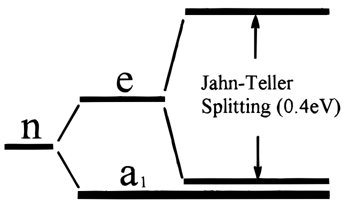


Figure 2. He I photoelectron spectra of $HOClO_3$ and $FOClO_3$.



Indeed, a Jahn–Teller splitting of about 0.4 eV is sufficient to produce the observed band of the PE spectrum of $HOClO_3$. That is to say, the area of the next PES peak (at 12.77 eV) is twice the area of the lowest IP peak (at 12.37 eV) in the first PES band of $HOClO_3$.

There is no splitting of the first PES band centered near 13.20 eV for $FOClO_3$. This may be explained as loss of C_{3v} symmetry in the ClO_3 atomic group of $FOClO_3$, a loss predicted by the ab initio geometry of $FOClO_3$ given in Table 1. The first PES band of $FOClO_3$ could be also attributed to electron ionization of the lone-pair orbitals in which three oxygen atoms in the ClO_3 atomic group of $FOClO_3$ hold dominant weight. The second PES band centered near 13.49 eV also arises from electron ionization of the orbitals associated with the oxygen atoms in $HOClO_3$. The third PES band centered near 15.09 eV is a result of orbital electron ionization from deeper valence shells.

An obvious difference between the ionization potentials of $HOClO_3$ and $FOClO_3$ is that those for $FOClO_3$ are always higher than those for $HOClO_3$. This fact is attributed to the large electronegativity of the fluorine atom and is consistent with the PES results for $HONO_2$ and $FONO_2$ obtained in this laboratory.[7,16]

TABLE 2: He I Experimental Ionization Potentials (eV) and the Eigenvalues (eV) Calculated by ab Initio SCF MO Calculation Using GAUSSIAN 94 at the 6-31G* Basis Set Level for Both $HOClO_3$ and $FOClO_3$ Molecules

	$HOClO_3$				$FOClO_3$			
	$-\epsilon_i$ (eV)	MO	character	IP (eV)	$-\epsilon_i$ (eV)	MO	character	IP (eV)
I_1	14.132	8a″(25)	n_{O_3}	12.37	14.839	9a″(29)	n_{O_3}	13.20
I_2	14.859	7a″(24)	n_{O_3}	12.77	15.555	8a″(28)	n_{O_3}	13.20
I_3	15.239	17a′(23)	n_{O_3}	12.77	16.087	20a′(27)	n_{O_3}	13.20
I_4	16.100	16a′(22)	σ_{O_4}	13.49	16.133	19a′(26)	σ_{O_4}	14.56
I_5	16.726	6a″(21)	π_{HOCl}	14.63	17.261	7a″(25)	π_{O_3ClO}	14.56
I_6	16.945	15a′(20)	σ_{HOClO_3}	15.09	17.602	6a″(24)	π_{FOClO_3}	15.80
I_7	18.104	5a″(19)	π_{HOClO_3}	15.09	17.603	18a′(23)	σ_{FOClO_3}	15.80
I_8	19.978	14a′(18)	σ	17.27	19.966	17a′(22)	σ	16.80

These intuitive PES assignments are supported by ab initio 6-31G* basis set calculations for both $HOClO_3$ and $FOClO_3$ molecules. The calculated ionization energies ($-\epsilon_i$) based on Koopmans' approximation[17] and the experimental ionization energies are listed in Table 2. The MOs associated with each band are designated according to their atomic and bonding characters. The experimental IPs are given in Table 2 in the form of overlapping band maxima since the observed bands are associated with the ionization of varying numbers of orbitals.

Table 2 shows that the characters of the HOMO 8a″(25), the SHOMO 7a″(24), and the 17a′(23) orbitals mainly embody the lone pairs of the three oxygen atoms in the ClO_3 atomic group of the $HOClO_3$ molecule and correspond to π and σ bonds. Ionization of these three orbitals should produce two sharp peaks with high intensity and low ionization potential (IP), because ionization of the lone-pair electrons usually leads to sharp peaks and a lower ionization potentials in these species. If the first sharp peak (at 12.37 eV) in the first PES band of $HOClO_3$ can be considered to be ionization of the HOMO 8a″(25), the second sharp peak (at 12.77 eV) in the first PES band of $HOClO_3$ is then assigned to ionizations of both the SHOMO 7a″(24) and the 17a′(23) orbitals because relative intensities are usually proportional to orbital degeneracies. Ionization of the 16a′(22) orbital leads to the second band centered near 13.49 eV of $HOClO_3$ because the second band has low intensity. If ionization of 6a″(21) leads to the shoulder centered near 14.63 eV in the third PES band of $HOClO_3$, the ionization of both 15a′(20) and 5a″(19) orbitals should lead to the peak centered near 15.09 eV in the third PES band of $HOClO_3$, because the peak has high intensity and is very wide. The assignment of the PES bands with low intensity in the high ionization region (>16.50 eV) of $HOClO_3$ is also given in Table 2. These assignments are consistent with the energy gaps obtained by computation.[18]

A similar assignment follows for the PES bands of $FOClO_3$. The 9a″(29), 8a″(28), and 20a′(27) orbitals have the lone-pair character of three oxygen atoms in the ClO_3 atomic group for $FOClO_3$ and correspond to the π and σ bonds. The ionization of these orbitals leads to a band with high intensity and low ionization potential. No splitting occurs in the first PES band of $FOClO_3$, because of the loss of the C_{3v} symmetry of the ClO_3 atomic group and the large electronegativity of fluorine. Ionization of both 19a′(26) and 7a″(25) orbitals should lead to the second PES band centered near 14.56 eV of $FOClO_3$, because the second PES band of $FOClO_3$ has high intensity in comparison with the second PES band of $HOClO_3$, and PES band intensity is usually proportional to the degeneracy of the ionized orbital. The 6a″(24) orbital is a π bond with dominant weight on the FO group. The electron ionization of both 6a″(24) and 18a′(23) orbitals should lead to the third PES band centered near 15.80 eV, which is of high intensity and narrow width, because the photoionization cross section of fluorine is larger than that of chlorine for He I radiation and the computed ionization energy (17.602 eV) for the 6a″(24) orbital is very close to the computed ionization energy (17.603 eV) for the 18a′(23) orbital. The assignment of the PES bands in the high-energy region (>16.50 eV) for $FOClO_3$ is also given in Table 2.

Thus, the assignments of the PES bands are consistent with the argument based on band shape, relative intensities, and ab initio calculations.

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