

**AB INITIO STUDY OF THE STRUCTURE AND SPECTROSCOPIC PROPERTIES  
OF HALOGENATED THIOPEROXY RADICALS**

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### 1. Introduction

Thioperoxy (XSO or XOS) radicals exist in a variety of chemical environments, and they have as a consequence drawn some interest. HSO, an important species in the chemistry of the troposphere, has been examined both experimentally [1-3] and theoretically [4, 5]. The halogenated (X = F, Cl or Br) peroxy species and isovalent thioperoxy species have been studied less, but they too are potentially interesting because oxidized sulfur species and halogen sources are present in the atmosphere [6]. Learning the fate of XSO and XOS radicals is important to understanding the atmospheric oxidation chemistry of sulfur compounds. Of these, FSO [7, 8] and ClSO [8, 9] are particularly interesting because they have been directly detected spectroscopically.

Recent studies [10, 11] in our laboratory on the photochemistry of thionyl halides (X<sub>2</sub>SO; where X = F or Cl) have suggested new ways to generate XSO species. The laser-induced photodissociation of thionyl fluoride, F<sub>2</sub>SO, at 193 nm and thionyl chloride, Cl<sub>2</sub>SO, at 248 nm is characterized by a radical mechanism [10, 11],



The structure of FSO has been characterized experimentally by Endo *et al.* [7] employing microwave spectroscopy. Using the unrestricted Hartree-Fock (UHF) self-consistent field (SCF) method, Sakai and Morokuma computed the electronic structure of the ground <sup>2</sup>A'' and the first excited <sup>2</sup>A' states of FSO [12]. Electron correlation was not taken into account in their study.

In a laser photodissociation experiment, Huber *et al.* identified ClSO mass spectrometrically [13]. ClSO has also been detected in low temperature matrices by EPR [9] and in the gas phase by far IR laser magnetic resonance [8]. Although the structure of FSO is known in detail, the only study, experimental or theoretical, of ClSO has been an *ab initio* HFSCF study by Hinchliffe [14]. Electron correlation corrections were also excluded from this study.

In order to better understand the isomerization and dissociation dynamics of the radical species, we have performed *ab initio* correlated studies of the potential energy surfaces (PES) of ClSO and its isomer ClOS at the QCISD(T)/6-31G\* level of theory [15]. For FSO and FOS, more extensive QCISD/6-311G(2df) calculations have been possible, and the results are summarized here.

### 2. Structure and spectroscopic properties of FSO and FOS in the ground <sup>2</sup>A'' state

The geometry optimizations and harmonic frequency analyses of the isomers FSO and FOS were done with the Gaussian92 suite of programs [16]. The importance of including d- and f-polarization functions in basis sets for accurate calculation of the equilibrium geometries of fluorine- and sulfur-containing species is documented [17], and adequate sets were employed. The equilibrium geometries and harmonic vibrational frequency analyses of the isomer radicals in the ground <sup>2</sup>A'' state were determined

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by the UHF method with QCISD electron correlation correction based on the UHF reference state. A “frozen core” exclusion of the inner shells from the QCISD calculations was adopted. The optimum geometry of the closed-shell FSO<sup>+</sup> ion was also computed with the same 6-31 1G(2df) basis at the QCISD level in order to obtain an accurate estimate of the adiabatic ionization energy of FSO.

Table 1 shows the optimized geometry of ground state FSO determined at the UHF/6-311G(2df) and QCISD/6-311G(2df) levels of theory. The results of our calculations on FSO are to be found, respectively, in the first and third rows. In their UHFSCF calculations, Sakai and Morokuma [12] computed the electronic structures of the ground <sup>2</sup>A'' and first excited <sup>2</sup>A' states of FSO. They employed 4-31 G basis sets and augmented them with s- and p-type Gaussian bond polarization functions. Their results are reproduced in the second row of Table 1 for comparison. To our knowledge, there has been no *ab initio* correlated study on this system prior to our own. Endo *et al.* [7] carried out a microwave spectroscopic study of ground state FSO and determined its geometry and fundamental vibrational frequencies. The fourth row of Table 1 displays the experimental bond lengths and bond angle.

Table 1. UHF–QCISD/6-311G(2df) optimized geometries of ground state FSO and FSO<sup>+</sup>

		F-S (Å)	S-O (Å)	∠ <sub>F-S-O</sub> (°)	Total energy (a. u.)
HF	This work	1.564	1.423	107.4	-571.8555
	Sakai <sup>a</sup>	1.560	1.443	107.9	
QCISD	This work	1.604	.454	108.0	-572.5015
Experiment <sup>b</sup>		1.6023	.4523	108.3	
FSO <sup>+</sup>					
HF	This work	1.472	1.361	110.8	-571.5045
	QCISD This work	1.510	1.401	111.5	

<sup>a</sup>Ref. [12]      <sup>b</sup>Experiment: Ref. [7]

The bond lengths and angle of FSO<sup>+</sup> at the UHF and QCISD levels are displayed in the last two rows of Table 1. Experimental work by Endo *et al.* [7] as well as *ab initio* SCF studies have shown FSO to be a n-radical with a spin-doublet ground <sup>2</sup>A'' state. The unpaired electron is in the SO antibonding  $\pi^*(4a'')$  orbital. FSO<sup>+</sup>, absent the unpaired electron in the antibonding orbital, exhibits shortened S–O and F–S bonds.

Accurate estimation of the adiabatic ionization potential of FSO is important to the interpretation of multiphoton ionization experiments. In such experiments, FSO<sup>+</sup> is produced by ionization via a highly excited valence or Rydberg state of FSO, a state which may well have almost the same nuclear configuration as does FSO<sup>+</sup>. At the QCISD level the difference in total energies of FSO (–572.5015 au.) and FSO<sup>+</sup> (–572.1517 a. u.) gives an accurate estimate (probably within  $\pm 0.1$  eV with the basis sets employed) of the adiabatic ionization potential of FSO. The computed estimate, 9.52 eV, falls into a range which indicates that two-photon ionization spectroscopy is feasible with commercially available lasers.

Table 2 presents the geometry of isomeric FOS radical, determined at the UHF/6-311G(2df) and QCISD/6-311G(2df) levels. There are no reported experimental data for the species. With FSO, QCISD

correlation correction brings the calculated bond lengths and angle closer to experimental, by 0.04 Å and 0.6°, respectively, than they are at the UHF level. In FOS, the effect of electron correlation on geometry is greater. A change of 0.15 Å in the F–O bond length is introduced by including correlation. Taking the FSO results as a guide, one expects the QCISD geometry of FOS to be accurate to within 0.01 Å and 1°, respectively, in the bond lengths and the angle. The S–O bond is longer and weaker in FOS than in FSO. The local minimum in the triatomic potential surface which corresponds to FOS lies 83.7 kcal/mole above the global, FSO, minimum. In two other thioperoxy radicals (XSO—XOS; where X = H and Cl) which have been studied, XSO is also more stable than XOS. In HSO—HOS [5], HSO is the most stable isomer by only 5.4 kcal/mol, whereas ClSO [14] is 42 kcal/mol more stable than ClOS. The uncertainty in the reported values of the enthalpy of formation of FSO leads to a range of values for the reaction  $F(^2P) + SO(X^3\Sigma^-) \rightarrow FSO(^2A'')$ . There is a corresponding range of reaction enthalpies reported, from 75 [18] to 86 kcal/mol [19], depending on the origin of the value for dissociation of  $FSO(^2A'')$  to  $F(^2P)$  and  $SO(X^3\Sigma^-)$  employed. The product  $F(^2P) + SO(X^3\Sigma^-)$  state is the lowest-dissociation asymptote correlating with the  $^2A''$  ground state of FSO or FOS. Assuming the upper limit value to be correct, the local minimum corresponding to the FOS isomer lies only a few kcal/mol below the dissociation asymptote leading to  $F(^2P) + SO(X^3\Sigma^-)$ .

Table 2. UHF–QCISD/6-311G(2df) optimized geometries of ground state FOS.

		F-O (Å)	S-O (Å)	$\angle_{F-S-O}$ (°)	Total energy (a. u.)
HF	This work	1.374	1.589	110.9	-571.7135
QCISD	This work	1.526	1.557	110.9	-572.3681

Table 3 displays the computed harmonic frequencies of FSO and the experimentally observed fundamentals [7]. The S–O and F–S harmonic frequencies computed at the QCISD/6-311G(2df) level are higher by 20 – 30 cm<sup>-1</sup> than the corresponding experimental values. The experimentally observed S–O stretching frequency in FSO is larger than the frequency (1148 cm<sup>-1</sup>) of isolated SO. The S–O bond length in FSO is also shorter by 0.03 Å than that in diatomic SO (1.481 Å). The S–O bond in FSO is strengthened by the presence of the electronegative fluorine, which reduces repulsion among the nonbonding electrons on oxygen and sulfur.

Table 3. QCISD/6-311G(2df) harmonic vibrational frequencies (in cm<sup>-1</sup>) of FSO and FOS.<sup>a</sup>

		$\omega_1$	$\omega_2$	$\omega_3$
FSO	Calculated	1240	791	413
	Observed <sup>b</sup>	1215	763	396
FOS	Calculated	911	491	362

<sup>a</sup>  $\omega_1, \omega_2,$  and  $\omega_3$  correspond, respectively, to the S–O and F–S stretching, and the F–S–O bending frequencies of FSO, and, respectively, to the S–O and F–O stretches and the F–O–S bend of FOS.

<sup>b</sup> Experiment: Ref. 7

The FOS harmonic frequencies appear in the last row of Table 3. There is a substantial difference in the S–O stretch of the two isomers; the frequency in FSO is larger by about 300 cm<sup>-1</sup> than in FOS. This difference is consistent with the finding that the S–O bond in FSO is shorter and stronger than in FOS. The computed F–S stretching frequency in FSO is also larger by about 300 cm<sup>-1</sup> than the F–O stretch in FOS. The low F–O frequency in FOS indicates that the bond is substantially weaker than the F–S bond in FSO and consistent with the fact that the potential energy surface is flat near the local FOS minimum region.

### 3. Structure and spectroscopic properties of CISO and CIOS in their ground <sup>2</sup>A" state

*A b initio* correlated calculations were performed on the <sup>2</sup>A" Cl–S–O potential surface in the region of the CISO + CIOS isomerization in order to understand the energetic of the process. About two hundred QCISD/6-31 G\* and QCISD(T)/6-31 G\* calculations were performed with the Gaussian92 system to map the surface in the region of interest.

Analysis of the computed potential surface has yielded minimum energy structures and spectroscopic properties of ground state CISO and CIOS. As with the FSO isomers, the optimum geometry of singly ionized, closed-shell CISO<sup>+</sup> was also computed. At the optimum geometry, a single QCISD(T) calculation was performed to more accurately estimate the total energy. Tables 4 and 5 show the QCISD/6-31G\* optimized geometries of ground state CISO, CISO<sup>+</sup> and CIOS.

CISO, like FSO, is bent with an unpaired electron in arc\* orbital. Similar to the case with FSO, removing the unpaired electron in CISO forms a CISO<sup>+</sup> ion with shorter S–O and S–Cl bond lengths. Mulliken population analysis reveals a rather large formal charge on the sulfur.

Table 4. QCISD/6-31G\* optimized geometries of ground state CISO and CISO<sup>+</sup>. Reported total energies are QCISD(T).

	Cl-S (Å)	S-O (Å)	∠ <sub>Cl-S-O</sub> (°)	Total energy (a. u.)
CISO	2.0864	1.4957	109.3	-932.26341
CISO <sup>+</sup>	1.9564	1.4500	112.0	-931.92706

Population analysis reveals some of the differences in charge distribution between CISO and CIOS, FSO and FOS, and between the chloro- and fluoro- pairs. In both CISO and FSO there is a relatively electropositive atom, S, flanked by a quite negative oxygen and halogen. In FSO the halogen is as electronegative as O, whereas in CISO it is much less so. Charge flows from the sulfur to the oxygen and halogen; in about equal amounts in FSO but more to O than Cl in CISO. The two molecules are therefore somewhat ionic, with large dipole moments. At the HF level the ordering of the dipole moments is FSO > CISO > FOS > CIOS. The S–O bond order in CISO is about 75% greater than the Cl–S. In FSO the S–O bond order is twice that of the F–S bond.

In CIOS and FOS the bond orders of the two bonds in each are equal, The effect on bonding, then, of having the most, rather than the least, electronegative atom in the center of each molecule is to reduce the S–O bond from a double to a single bond. There are differences in the actual details of the charge distributions in the two species. In CIOS a very electronegative atom is flanked by two larger

atoms of roughly equal **electronegativity**, while in FOS there is a relatively electropositive atom at one **end** of the molecule, with two highly electronegative atoms bonded to each other at the other end. **The** charge on the sulfur, as the **Mulliken** gross atomic population, is positive and the same in both molecules. It is reduced in magnitude from the values for FSO and CISO. In FOS, F and O both carry the same negative charge, smaller in magnitude than the charges on those atoms in FSO, and reflecting the fact that they are bonded to each other. In CIOS the central oxygen carries quite a large negative charge; Cl is positive to only a slightly lesser extent than S.

Table 5. Optimized geometry of CIOS.

	Cl-O (Å)	o-s (Å)	$\angle_{\text{Cl-O-S}}$ (°)	Total energy (a. u.)
QCISD	1.7893	1.6331	116.7	-932.19671*

\* Total energy computed at the QCISD(T)/6-31 G\* level of theory.

Table 6 shows the harmonic frequencies of the two isomers. The S–O stretch in CIOS is about  $300\text{cm}^{-1}$  lower in energy than it is in CISO, exactly as the corresponding frequencies differ in the FSO—FOS pair (see Table 3). The lower frequency reflects the weakness of the S–O bond in XOS relative to XSO which has been cited above. However, the Cl–O stretch in CIOS is about  $100\text{cm}^{-1}$  higher in energy than is the Cl–S stretch in CISO. In this pair of frequencies the CISO—CIOS pair reverses the tendency seen in FSO—FOS. The best **explanation** of the reversal **lies** in the contrast in atomic **electronegativities** of the atoms involved in the Cl–S, Cl–O, F–S and F–O bonds discussed above.

Table 6. Harmonic frequencies ( $\text{cm}^{-1}$ ) for the CISO radical and its isomer CIOS determined at the QCISD/6-31G\* level of theory.\*

	$\omega_1$	$\omega_2$	$\omega_3$
CISO	1098	479	294
CIOS	771	602	309

\*  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  correspond, respectively, to the harmonic S–O and Cl–S stretches and the Cl–S–O bend in CISO. For CIOS, they correspond to the S–O and Cl–O stretching and Cl–O–S bending frequencies.

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