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A theoretical study of high electron affinity sulfur oxyfluorides: SO_3F, SO_2F_3, and SOF_5

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Abstract

Gaussian-2 theory was used to study a series of sulfur oxyfluorides that have exceptionally high electron affinities (EAs). Optimized geometries were computed for SO_3F, SO_2F_3, SOF_5, and their corresponding anions at the MP2(full)/6-311+G(d) level of theory. Both SO_3F and SOF_5 are found to be stable with respect to dissociation, while SO_2F_3 is metastable with respect to SO_2F_2+F. In all cases, electron attachment results in a shortening of one long SO bond within the molecule and a corresponding increase in the remaining SF and SO bonds; a significant portion of the excess charge is accommodated in an SO bonding orbital. Harmonic vibrational frequencies with IR and Raman intensities were computed for all species, and the calculated vibrational spectra of SOF_5^- and $SO_2F_3^-$ are compared to the reported experimental spectra. The EAs of SO_3F, SO_2F_3, and SOF_5 are found to be 5.53, 5.50, and 5.14 eV, respectively, all well exceeding the threshold of 3.6 eV that defines a superhalogen species. The corresponding anion vertical detachment energies and neutral vertical attachment energies are also reported here. The calculated EA of SO_3F is discussed in relation to the gas-phase acidity of FSO_3H. The homolytic bond dissociation energy of FSO_3H is found to differ significantly from the previous estimate, suggesting the previous experimental estimate for the EA of SO_3F [J. Am. Chem. Soc. 114 (1992) 4299] be revised upward from 4.8 to 5.2 eV. (Int J Mass Spectrom 218 (2002) 207–215)
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1. Introduction

The term "superhalogen" is used to describe polyatomic systems whose electron affinity (EA) exceeds that of the most electronegative halogen atom, i.e., the EA is greater than 3.6 eV. Superhalogens of the type MX_{n+1} (where X is a halogen atom and n is the maximum formal valency of the central atom, M) have been the subject of numerous theoretical and experimental studies because their corresponding anions are widely used as counterions in solid and gas-phase chemistry [1]. In this study we report the first high-level theoretical investigation of a closely related class of superhalogens of the form MO_nX_{m+1}, where $2n+m$ represents the maximum formal valency of the central atom. The oxygen atom essentially substitutes for two halogen atoms. All the species included in this study contain sulfur as the central atom, M: SOF_5, SO_2F_3, and SO_3F.

The SO_3F radical has previously been reported to have a very high EA. Viggiano et al. [2] estimated the EA to be 4.8 eV from gas-phase acidity bracketing experiments. Not surprisingly, the corresponding SO_3F^- anion is thought to be relatively inert to chemical attack; methane/oxygen flames doped

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with sulfur/fluorine additives were found to rapidly produce SO_3F^- which then persists throughout the burnt gas region of the flame [3]. There have been no previous estimates made for the EA of the other two radicals in this series, SO_2F_3 and SOF_5, despite the fact that their corresponding anions, SOF_5^- and $SO_2F_3^-$, have been observed experimentally. The SOF_5^- anion, which is isoelectronic with SF_6, has been observed as a long-lived species in SF_6/H_2O plasmas [4,5]. While it has been the subject of some previous study [6–10], the corresponding neutral EA has not been reported, nor has a high-level geometry calculation of either the neutral or the anion been reported. The $SO_2F_3^-$ anion, which is isoelectronic with the well-known ClO_2F_3, has been reported in F^- transfer experiments with SO_2F_2 [11–13]. However, the structure and energetics of SO_2F_3 and $SO_2F_3^-$ have not been explored in detail.

In this study, we report Gaussian-2 (G2) calculations for three sulfur oxyfluoride superhalogen species (SO_3F, SO_2F_3, SOF_5) and their corresponding anions. Equilibrium configurations, charge distributions, and harmonic frequencies with IR and Raman intensities are reported, together with electron affinities, vertical attachment energies, and vertical detachment energies.

2. Computational details

Calculations were carried out using the G2 procedure of the G98W program system [14]. This method yields extrapolated total energies corresponding to a QCISD(T)/6-311+G(3df,2p) calculation for geometries optimized at the MP2(full)/6-31G(d) level of theory with zero-point energies (ZPEs) computed at the HF/6-31G(d) level and scaled by 0.893. The stability of all wave functions was confirmed. In order to obtain more accurate geometries and frequencies than used in G2 theory, these quantities were also calculated at the MP2(full)/6-311+G(d) level of theory, principally to gain the benefit of diffuse functions in the basis set. Atomic charge distributions were determined using the natural population analysis method [15] at the MP2(full)/6-311+G(d) level. EAs were determined as the difference in energy between the neutral molecule and the molecular anion with both species in their ground electronic, vibrational, and rotational states. The G2 method is reported to yield EAs accurate usually to within 0.070 eV [16]. Vertical detachment energies (VDEs) were determined as the minimum energy required to eject the electron from the ground state anion (0 K) without allowing a change to occur in the anion equilibrium geometry. Vertical attachment energies (VAEs) were determined as the difference in energy between the ground state neutral molecule (0 K) and the molecular anion without allowing a change in the neutral equilibrium geometry. For SO_2F_3 and SOF_5, the vertical transitions intersect the neutral (VDE) or anion (VAE) potential surface in a region where there are many low frequency vibrations, so the actual VDE or VAE should agree with the calculated values within the expected accuracy of 0.1 eV. For SO_3F, the calculated VDE was 0.25 eV below the zero-point vibrational level, so the minimum VDE in that case is the same as the adiabatic EA. In the course of this work, the homolytic bond strength for FSO_3H was also calculated as the enthalpy difference between FSO_3H and the sum of FSO_3 and H.

3. Results and discussion

3.1. Structure and thermodynamic stability

The minimum energy structures for SO_3F, SO_2F_3, and SOF_5, and their corresponding anions, calculated at the MP2(full)/6-311+G(d) level of theory, are shown in Fig. 1. Obtaining an accurate description of anions and systems containing lone pairs of electrons is generally found to require treatment of electron correlation and the use of basis sets containing diffuse functions. For the sulfur oxyfluorides considered here, inclusion of diffuse functions in the basis set results in shorter SO bonds, longer SF bonds (particularly in the anion structures), and little to no change in the bond angles.

The anions are all higher-order symmetry species than their corresponding neutrals. SOF_5, SO_2F_3, and

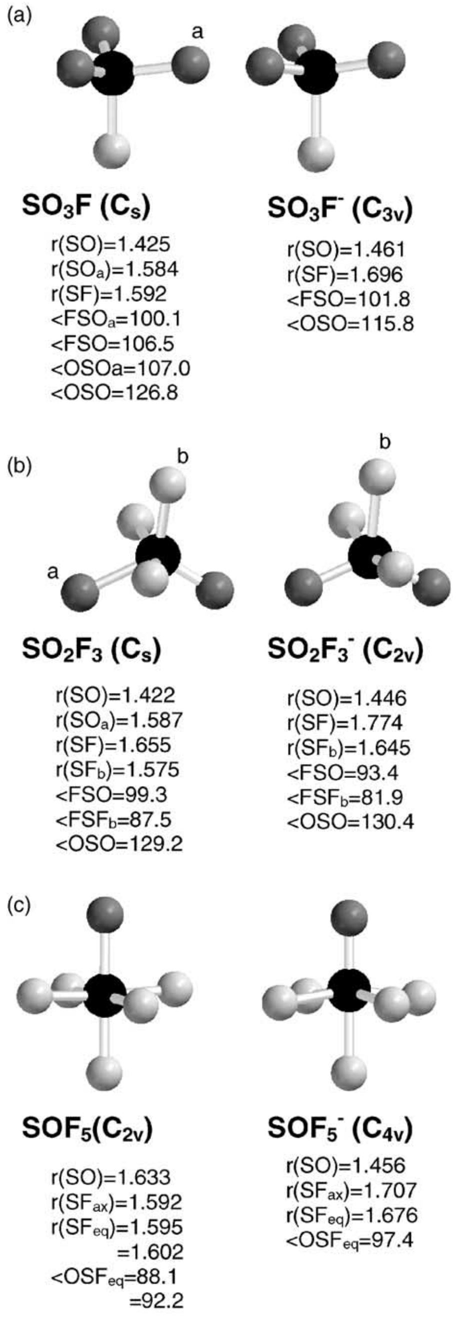

Fig. 1. Structural parameters for (a) SO_3F and SO_3F^-, (b) SO_2F_3 and $SO_2F_3{}^-$, and (c) SOF_5 and $SOF_5{}^-$, calculated at the MP2(full)/6-311+G(d) level of theory.

SO_3F are C_{2v}, C_s, and C_s, structures, respectively, while their anions are of C_{4v}, C_{2v}, and C_{3v} symmetries, respectively. At the MP2(full)/6-311+G(d) level of theory, the sulfur–oxygen bond lengths for all three anions are 1.446–1.461 Å, characteristic of S=O double bonds [17]. In contrast, the neutral molecules each have one significantly longer sulfur oxygen bond, 1.584–1.633 Å, which more closely resembles the single S–O bond distances in HSO_4 and H_2SO_4 [18]. This is consistent with the fact that for all three neutral radicals, the spin density is localized on a single oxygen atom.

The primary structural changes that occur in each neutral species upon electron attachment include a dramatic shortening of the one long SO bond within the molecule (i.e., an increase in the SO bond multiplicity) and a corresponding lengthening of the remaining SF and SO bonds, consistent with the qualitative expectations of Klyagina et al. [10]. As shown in Table 1, a natural population density charge distribution

Table 1
Charge distribution analysis from the natural population density method at the MP2/6-311+G(d) level of theory with geometries optimized at MP2(full)/6-31G(d) level

Atom	Neutral	Anion	Change upon e^- attachment
SO_3F			
S	2.38	2.44	0.06
O	−0.36	−0.96	−0.60
O	−0.78	−0.96	−0.18
O	−0.78	−0.96	−0.18
F	−0.46	−0.57	−0.11
SO_2F_3			
S	2.43	2.46	0.03
O	−0.29	−0.90	−0.61
O	−0.77	−0.90	−0.13
F	−0.47	−0.58	−0.11
F	−0.47	−0.58	−0.11
F	−0.42	−0.50	−0.08
SOF_5			
S	2.45	2.48	0.03
O	−0.29	−0.95	−0.66
F	−0.43	−0.51	−0.08
F	−0.43	−0.51	−0.08
F	−0.44	−0.51	−0.07
F	−0.44	−0.51	−0.07
F	−0.42	−0.50	−0.08

analysis for each system indicates over 60% of the excess charge is accommodated in a SO bonding orbital. The SO bonds within the anions are all characteristic of double bonds.

Previous reports of the anion structures include an early calculation of SOF_5^- by Rode [7] that indicated an anion SO bond length of 1.64 Å, which is undoubtedly too high. Recently, Steudel and Otto [19] reported the structure of SO_3F^- calculated at the MP2/6-311+G(d) level. Comparing their results to the present calculations performed using the identical basis set demonstrates that the only structural parameter significantly affected by the frozen-core approximation of Steudel and Otto is the S–F bond length, which changes by ∼2%. Although an experimental structure of SO_3F^-, obtained by X-ray crystallography of the lithium salt, has been reported by Zak and Kosicka [20], the salt structure is known to be of C_s symmetry, not C_{3v} like the gas-phase ion. The crystal structure indicates SO bond lengths of 1.424 and 1.455 Å and a SF bond length of 1.555 Å, significantly shorter than the calculated internuclear distances in isolation. Presumably, the presence of multiple Li^+ cations in the crystal distorts the symmetry and polarizes the anion, thereby shortening the SF bond in particular.

At the G2 level of theory, both SO_3F and SOF_5 neutrals were found to be thermodynamically stable with respect to dissociation. Homolytic SF bond dissociation energies, D°[S–F], for SO_3F and SOF_5 are calculated to be 1.69 and 1.14 eV, respectively. The minimum energy structure for the SO_2F_3 neutral, however, was found to be metastable with respect to dissociation to $SO_2F_2 + F$ by 0.26 eV. Attempts to locate the transition state at the HF level were unsuccessful. Thus, we cannot say how much energy is required for the dissociation. The dissociation energy determined here for SOF_5 is within 0.1 eV of the reported experimental value [21]. Experimental values have not been reported for SO_3F or SO_2F_3.

3.2. Vibrational spectra

Harmonic vibrational frequencies with infrared and Raman intensities for SO_3F, SO_2F_3, SOF_5, and their corresponding anions calculated at the MP2(full)/6-311+G(d) level of theory are reported in Table 2 with no empirical scaling. Note that relative values of the intensities are considered more reliable than the actual computed values. All three anions and two of the neutrals display intense IR S=O stretching frequencies in the range 1050–1500 cm^{-1}. In contrast, vibration of the SO single bond that is present in the neutral species is closely coupled with one fluorine atom, yielding OSF stretching frequencies in the range from 750 to 920 cm^{-1}. Anion modes involving motion of the SF bonds yield strong IR features in the 490–720 cm^{-1} region, while similar motions in the neutral species result in strong IR features at 730–900 cm^{-1}, presumably owing to the shorter SF bonds that exist in the neutrals (see Fig. 1).

A detailed comparison of the frequencies obtained utilizing different levels of theory or different basis sets was made for SOF_5^-. Bond lengths and vibrational frequencies calculated at the MP2(full)/6-311+G(d), MP2(full)/6-31G(d), HF/6-311+G(d), and HF/6-31G(d) levels of theory are shown in Table 3. Recommend scaling factors [22] for the MP2(full)/6-31G(d) and HF/6-31G(d) frequency calculations are 0.9427 and 0.8929, respectively. Scaling factors for MP2(full)/6-311+G(d) and HF/6-311+G(d) frequency calculations have not been reported. As indicated previously, treatment of electron correlation and inclusion of diffuse functions has little effect on the SO bond length, while it significantly lengthens the SF bonds. Accordingly, the frequency of the SO stretching mode in SOF_5^-, ν_1, decreases only 3% between the lowest and highest levels of theory in this study, while other modes involving SF motions decrease by 16–37%.

Experimental vibrational frequencies and assignments reported previously for SOF_5^- and $SO_2F_3^-$ are shown in Table 4. Christe et al. [8] have reported the IR and Raman spectra of SOF_5^-, as crystalline $CsSOF_5$. Eleven modes from the combined spectra were assigned to SOF_5^- by assuming a square-bipyramidal anion structure of C_{4v} symmetry. Comparing the unscaled MP2(full)/6-311+G(d) frequencies with the experimental frequencies reported by Christe et al.

Table 2
Unscaled harmonic vibrational frequencies, assignments, and IR and Raman (*R*) intensities calculated at the MP2(full)/6-311+G(d) level of theory

Species	Assignment		Frequency (cm^{-1})	IR ($km\,mol^{-1}$)	*R* ($Å^4\,amu^{-1}$)
SOF_5^- (C_{4v})	A_1	ν_1	1222	425	9.2
		ν_2	626	149	24
		ν_3	566	4	5.9
		ν_4	446	24	5.5
	B_1	ν_5	402	0	1.7
	B_2	ν_6	471	0	8.0
		ν_7	329	0	0.0
	E	ν_8	720	1147	0.3
		ν_9	542	3	3.6
		ν_{10}	498	0	5.6
		ν_{11}	287	1	0.0
SOF_5 (C_{2v})	A_1	ν_1	919	345	0.3
		ν_2	705	4	20.9
		ν_3	622	2	2.1
		ν_4	592	3	4.3
		ν_5	568	47	0.3
		ν_6	321	0	0.0
	A_2	ν_7	473	0	1.8
	B_1	ν_8	876	461	0.1
		ν_9	568	30	0.0
		ν_{10}	504	0	2.6
		ν_{11}	342	0	0.0
	B_2	ν_{12}	896	431	0.2
		ν_{13}	540	33	0.3
		ν_{14}	426	5	1.4
		ν_{15}	295	0	0.0
$SO_2F_3^-$ (C_{2v})	A_1	ν_1	1130	161	26.1
		ν_2	682	203	21.0
		ν_3	503	2	6.9
		ν_4	388	0	10.2
		ν_5	269	0	1.4
	A_2	ν_6	486	0	3.4
	B_1	ν_7	618	306	0.1
		ν_8	492	388	0.7
		ν_9	477	46	2.4
	B_2	ν_{10}	1396	404	3.1
		ν_{11}	511	39	2.8
		ν_{12}	220	0	0.6
SO_2F_3 (C_s)	A'	ν_1	1403	236	11.0
		ν_2	895	192	2.1
		ν_3	754	69	19.3
		ν_4	558	8	8.3
		ν_5	510	32	3.9
		ν_6	502	34	4.6
		ν_7	281	0	1.5
		ν_8	215	0	0.8
	A''	ν_9	733	424	0.6
		ν_{10}	555	22	2.8
		ν_{11}	476	0	2.2
		ν_{12}	413	32	0.1

Table 2 (*Continued*)

Species	Assignment		Frequency (cm^{-1})	IR ($km\,mol^{-1}$)	R ($Å^4\,amu^{-1}$)
SO_3F^- (C_{3v})	A_1	ν_1	1053	63	43.6
		ν_2	647	302	5.2
		ν_3	494	17	9.0
	E	ν_4	1290	878	12.1
		ν_5	554	85	8.6
		ν_6	369	0	4.7
SO_3F (C_s)	A′	ν_1	1229	93	51.4
		ν_2	822	198	6.4
		ν_3	746	87	7.4
		ν_4	516	38	4.8
		ν_5	511	21	5.1
		ν_6	347	0	2.2
	A″	ν_7	1486	238	17.9
		ν_8	464	31	2.5
		ν_9	271	5	0.2

[8] shows agreement within 70 cm^{-1} for the majority of modes; however, several modes are found to differ by up to 140 cm^{-1}, and there are several notable differences in the scaled Raman intensities. The highest frequency band within the crystalline $CsSOF_5$ spectrum at 1154 cm^{-1}, assigned to the SO stretching mode of SOF_5^-, is 68 cm^{-1} lower than the calculated gas-phase SO stretching frequency of 1222 cm^{-1}. A normal coordinate analysis by Christe et al. [8], which yielded a force constant smaller than those generally found for S=O double bonds, led the authors to report an SO bond order of 1.5 for SOF_5^-. However, the calculated gas-phase SO bond lengths and stretching force constants are consistent with a double bond. A comparison of the calculated gas-phase frequencies for modes involving SF motions with those reported for crystalline SOF_5^- demonstrates the gas-phase frequencies are consistently lower. Differences between the gas-phase and crystalline spectra suggest a significant matrix effect, wherein the crystalline SF bonds are shorter and stronger than those in the gas-phase species, while the crystalline SO bond is longer and

Table 3
Bond lengths (Å) and unscaled harmonic vibrational frequencies (cm^{-1}) for SOF_5^- at various levels of theory

	MP2(full)/6-311+G(d)	MP2(full)/6-31G(d)	HF/6-311+G(d)	HF/6-31G(d)
S–O	1.456	1.472	1.441	1.452
S–F_e	1.676	1.661	1.611	1.613
S–F_a	1.707	1.685	1.645	1.640
ν_1	1222	1240	1240	1259
ν_2	626	714	769	807
ν_3	566	588	661	657
ν_4	446	558	540	611
ν_5	402	423	488	483
ν_6	471	566	577	627
ν_7	329	344	386	385
ν_8	720	856	870	945
ν_9	542	575	651	650
ν_{10}	498	521	583	580
ν_{11}	287	299	347	343

F_e and F_a denote equatorial and axial F atoms, respectively.

Table 4
Experimental vibrational frequencies and assignments for SOF_5^- and $SO_2F_3^-$

Ion	Assignment		Frequency	IR	Raman	Mode
SOF_5^- (C_{4v})[a]	A_1	ν_1	1154 (1222)	vs	1 (3.8)	ν(SO)
	A_1	ν_2	722 (626)	vs	0.2 (10)	ν(SF)
	A_1	ν_3	697 (566)	m	10 (2.5)	$\nu_{sym}(SF_4)$
	A_1	ν_4	506 (446)	s	1 (2.3)	δ_{sym}(out-of-plane SF_4)
	B_1	ν_5	541 (402)		3 (0.7)	ν_{sym}(out-of-phase SF_4)
	B_1	ν_6	472 (471)		0.2 (3.3)	δ_{asym}(out-of-plane SF_4)
	B_2	ν_7	452 (329)		0.9 (0.0)	δ_{sym}(in-plane SF_4)
	E	ν_8	780 (720)	vs	0.1 (0.1)	$\nu_{asym}(SF_4)$
	E	ν_9	607 (542)	s	2.2 (1.5)	$\delta(OSF_4)$
	E	ν_{10}	530 (498)	sh	2 (2.3)	$\delta(FSF_4)$
	E	ν_{11}	325 (287)	mw	0.0 (0.0)	δ_{asym}(in-plane SF_4)
$SO_2F_3^-$ (C_{2v})[b]	A_1	ν_1	1130	vs		$\nu_{sym}(SO_2)$
	A_1	ν_2	810	vs		ν(SF)
	A_1	ν_4	649	vs		$\nu_{sym}(SF_2)$
	B_1	ν_7	925	vs		$\nu_{asym}(SF_2)$
	B_2	ν_{10}	1408	s		$\nu_{asym}(SO_2)$

Unscaled MP2(full)/6-311+G(d) frequencies and normalized Raman intensities are shown in parenthesis for comparison.
[a] Christe et al. [8].
[b] Garber and Ault [13].

weaker compared to the gas-phase ion, both owing to the polarizing effects of the Cs^+ counterions.

The infrared spectrum of $SO_2F_3^-$, ion paired with Cs^+ in an argon matrix, has been reported by Garber and Ault [13]. Assuming a trigonal-bipyramidal anion structure of C_{2v} symmetry, five bands were assigned to the $F_3SO_2^-$ anion as shown in Table 4. Four of the five assigned bands correspond to intense bands in the calculated infrared spectrum; however, the band observed at 649 cm^{-1} and assigned ν_4 more likely corresponds to the intense ν_8 band expected at 492 cm^{-1} since the ν_4 band is expected to be only a very weak feature in the infrared spectrum. The experimental symmetric and antisymmetric SO stretching frequencies at 1130 and 1408 cm^{-1}, respectively, are in excellent agreement with the unscaled MP2(full)/6-311+G(d) values shown in Table 2. However, for the remaining modes involving SF motions, the experimental frequencies are 128–307 cm^{-1} higher than the calculated values. Either this level of theory does not provide an accurate description of the SF bonds within $SO_2F_3^-$, or the SF bonds in the anion are significantly perturbed in the matrix environment by the presence of Cs^+ counterions, while the SO bonds are unaffected.

3.3. EA, VDE, VAE

Neutral EAs and VAEs and anion VDEs, calculated using the G2 method, are reported in Table 5. All three neutral molecules are found to have exceptionally high EAs, well above the 3.6 eV threshold needed to be classified as superhalogens. The EAs of SO_3F, SO_2F_3, and SOF_5 are 5.53, 5.50, and 5.14 eV, respectively. Such high EAs are noteworthy because very few compounds comprised solely of main group atoms are reported to have EAs over 5 eV. (Note, nearly all species with EAs in this range are transition metal fluorides such as PtF_6 or solvated halide ion clusters such as $I^-(H_2O)_n$ [23,24].) Gutsev et al. [1] calculated the EAs of LiF_2 and NaF_2 to be 5.45 and 5.12 eV, respectively, and Wang and coworkers [18,25] reported the EAs of ClO_4 and SO_4 to be 5.25 and 5.1 eV, respectively.

Table 5
G2 adiabatic EA, anion VDE, and VAE (eV)

	EA	VDE	VAE
SO_3F	5.53	5.53	5.08
SO_2F_3	5.50	6.29	3.83
SOF_5	5.14	5.98	4.53

In addition, SO_3CF_3, an analog of SO_3F where a trifluoromethyl group is substituted for the fluorine atom, is reported to have an EA > 5.3 eV [26].

Only one previous EA estimate exists for any of these species. Viggiano et al. [2] experimentally bracketed the gas phase acidity (GPA) of FSO_3H at 368 K and used this result to estimate EA(SO_3F) as 4.8 ± 0.2 eV based on the following relation:

$$\mathrm{GPA} = I(\mathrm{H}) + D^{\circ}[\mathrm{A}\cdots\mathrm{H}] - \mathrm{EA}(\mathrm{A}) \qquad (1)$$

where GPA is the enthalpy of deprotonation, I(H) is the ionization potential of H, and $D^{\circ}[\mathrm{A}\cdots\mathrm{H}]$ is the acid bond strength. The EA of SO_3F was estimated from Eq. (1) using the reported literature estimate for $D(\mathrm{FSO_3}\cdots\mathrm{H})$ of 440 kJ mol^{-1} [27]. However, in the course of this work, the neutral bond dissociation energy, $D^{\circ}[\mathrm{FSO_3}\cdots\mathrm{H}]$, was calculated at the G2 level to be 482 kJ mol^{-1}, which differs from the previous estimate by a substantial 42 kJ mol^{-1}. The EA estimate of Viggiano et al. [2] should be revised upward by this amount. Using the calculated bond dissociation energy, which we believe to be more reliable, results in a revised estimate for EA(SO_3F) of 5.2 ± 0.2 eV, which is in excellent agreement with the present calculations. Equivalently, the GPA of FSO_3H calculated here is in excellent agreement with the experimental result of Viggiano et al. [2].

The relationship between the EA, the VDE, and the VAE is shown in Fig. 2 in a schematic adapted from Christophorou [28]. Both the EA and the VDE are shown as positive values in Fig. 2. Note that EA(AX) $\leq$ VDE(AX^-) with these values being equal only if the equilibrium internuclear separations for AX and AX^- are nearly the same. The VAE can be either a positive or a negative value, depending on the exact nature of the surfaces. A positive value for the VAE is used to denote situations as shown in Fig. 2a. As expected, the calculated VDEs for SO_3F^-, $SO_2F_3^-$, and SOF_5^- are all greater than or equal to the corresponding neutral EAs. The VDE of $SO_2F_3^-$ and SOF_5^- are both approximately 0.8 eV larger than the corresponding neutral EA values, while the VDE of SO_3F^- is exactly equal to the corresponding neutral EA. The calculated VAEs for SO_3F, SO_2F_3, and SOF_5 are all positive values as defined in Fig. 2, ranging from 3.8 to 5.1 eV, suggesting a situation similar to that shown in Fig. 2a.

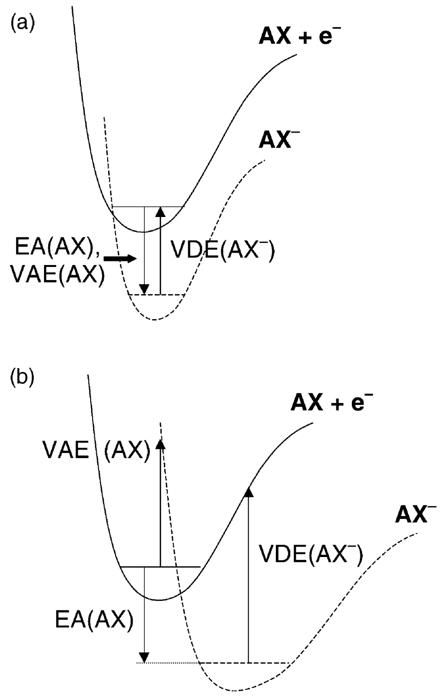

Fig. 2. Schematic representations of EA(AX), VDE(AX^-), and VAE(AX), as adapted from Christophorou [28]. EA(AX) and VDE(AX^-) are shown as positive values in both (a) and (b) while VAE(AX) is shown to be a positive value in (a) and a negative value in (b).

Experimental photodetachment studies of SO_3F^-, $SO_2F_3^-$, and SOF_5^- would be instrumental in confirming the EA results presented in this study. Because the EA of $SO_3F \sim$ VDE of SO_3F^-, the photodetachment spectrum of that ion should be characterized by a dominant origin band. In addition, it is anticipated that all three photodetachment spectra will show features attributed to S=O stretching motions, corresponding to the changing S–O bond length upon electron detachment.

4. Conclusion

The EAs of the sulfur oxyfluoride radicals SO_3F, SO_2F_3, and SOF_5, calculated using G2 theory, were found to well exceed the 3.6 eV threshold that defines a superhalogen species. Two of the neutrals (SO_3F and SOF_5) are found to be stable with respect to dissociation, while SO_2F_3 is metastable with respect to $SO_2F_2 + F$. In the corresponding anions, a significant portion of the excess electron is accommodated in an oxygen bonding orbital, resulting in a shortening of the one long SO bond that is found in the neutral species.

Harmonic vibrational frequencies with IR and Raman intensities were computed for all species at the MP2(full)/6-311+G(d) level of theory. The calculated vibrational spectra of SOF_5^- and $SO_2F_3^-$ were compared to the experimental spectra, and differences are consistent with the crystalline and matrix isolated species having stronger SF bonds and somewhat weaker SO bonds compared to the gas-phase species, presumably owing to the presence of counterions.

The homolytic bond dissociation energy, $D^\circ[FSO_3 \cdots H]$, of FSO_3H was calculated at the G2 level and was found to differ significantly from the previous estimate, suggesting the previous experimental estimate [1] of $EA(SO_3F)$ be revised upward from 4.8 to 5.2 eV.

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