

Vibrational Spectra and Structural Aspects of Fluorosulfites

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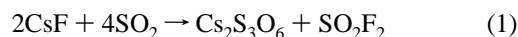
The Raman and infrared spectra of the fluorosulfites of K^+ , Rb^+ , Cs^+ , NH_4^+ , and Me_4N^+ have been examined. Previous assignment of the fundamental vibrations is revised, and an ab initio study of the SO_2F^- anion is presented. For the pyramidal anion of symmetry C_s , distances of $r(S-O) = 1.458 \text{ \AA}$ and $r(S-F) = 1.698 \text{ \AA}$ have been calculated. The heat of formation of Me_4NSO_2F (-14.0 kcal/mol) was derived from the dissociation pressure of the salt. In addition, the lattice energy of Me_4NF (159.2 kcal/mol) was calculated from a thermochemical cycle. The thermochemical data are discussed in terms of reactivity of the fluorides and stability of the fluorosulfites.

Introduction

Fluorosulfites were mentioned for the first time by Seel and Meier in the course of their investigation of the lead chamber process.¹ Later, Seel et al. described the preparation of $Me_4N^+SO_2F^-$ by the reaction of sulfur dioxide with naked fluoride (Me_4NF) and reported the first studies of the Na^+ , K^+ , Rb^+ , Cs^+ , and Me_4N^+ salts by X-ray powder patterns.^{2,3} In the case of the potassium salt, similarities to $KClO_3$ were found, but no structural data were obtained. The examination of the dissociation pressure of fluorosulfites was followed by the first reported IR spectrum of a fluorosulfite salt (KSO_2F).^{4–6} Robinson et al. reported the IR spectra of the K^+ , Rb^+ , Cs^+ , and NMe_4^+ salts and calculated force constants for the fluorosulfite ion.⁷ The results seem to be consistent with the work of Seel and Boudier,⁶ but the spectra exhibit three additional bands in the region between 600 and 1100 cm^{-1} and one at 1230 cm^{-1} , all attributed to combination tones. However, the next spectroscopic studies were reported 22 years later by Moock et al., who described the preparation of NH_4SO_2F .⁸ Despite the fact that fluorosulfite is the smallest fluoroxy sulfur anion, no work has been done to obtain the geometric parameters by theoretical investigations.

This lack of structural parameters for the SO_2F^- anion was surprising since KSO_2F was proposed as *activated fluoride* for a long time.^{9,10} In fact, besides the investigations by Seel et al.,^{2,3} it was used for only a few syntheses.^{11–17} Furthermore,

we found in the course of our investigations of alkali metal fluoride catalyzed reactions that fluorosulfites, which are readily formed in the presence of traces of sulfur dioxide, act as deactivators. This apparent contradiction and a recently found unusual reaction of CsF with SO_2 enhanced by ultrasound (eq 1)¹⁸ gave rise to investigations of the fluorosulfinate salts.



Furthermore, the reversible reaction of fluorides with SO_2 enables us to study the differences in the series KF , RbF , CsF , and Me_4NF , taking thermochemical parameters into account.

Experimental Section

Apparatus and Materials. All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard vacuum line. The alkali metal fluorides were dried thoroughly and crushed in a drybox under nitrogen. NH_4F was prepared from dry HF^{19} and NH_3 , since attempts to purify commercially available NH_4F by the method of Moock et al. gave a mixture of NH_4F and NH_4HF_2 .⁸ Me_4NF was obtained by the known literature method.²⁰ SO_2 (Messer Griesheim) was dried over CaH_2 . (*Caution! Anhydrous HF causes skin burning and irreparable damages! Fluorides and fluorosulfites are toxic!*)

The Raman spectra were recorded on a T64000 (ISA) using an argon ion laser (Spectra Physics) at 514.5 nm. The infrared spectrometer and sample preparation were described previously.¹⁹ The elemental analysis of fluoride and sulfur (as SO_4^{2-}) was carried out by ion chromatography of samples dissolved in water and oxidized with iodine.

Preparation of the Fluorosulfites. A 500 mg sample of carefully dried alkali metal fluoride (KF , RbF , CsF) was placed in a dried glass tube, and 5 g of SO_2 was condensed into the tube at $-196 \text{ }^\circ\text{C}$. The sealed glass tube was warmed to room temperature. The reaction proceeded upon thawing in a few minutes. The mixture was stirred

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for 1 day to ensure complete reaction. Excess SO₂ was pumped off at dry ice temperature. The increase in weight and the elemental analyses of the white solids indicated quantitative yields in the cases of RbSO₂F and CsSO₂F, but ca. 85% yield for KSO₂F. Quantitative yields of KSO₂F were obtained using KF that was prepared by thermal decomposition of the 85% KSO₂F at 140 °C in high vacuum. Further characterization of the obtained compounds was carried out by vibrational spectroscopy.

NH₄SO₂F and Me₄NSO₂F were prepared by the same procedure as CsSO₂F, but the reaction mixture was warmed to -40 °C. The yields were quantitative. The fluorosulfites hydrolyze rapidly upon contact with moisture.

Dissociation Pressure of Me₄NSO₂F. Me₄NSO₂F decomposes slowly under static SO₂ pressure at temperatures around 100 °C. The decomposition proceeds under formation of Me₄NSO₃F, Me₄NF, and sulfur. Besides SO₂, small traces of Me₃N, CH₃F, and SO₂F₂ were found in the gas phase. At temperatures below 100 °C only dissociation of Me₄NSO₂F under formation of the starting materials occurs. The SO₂ pressure of Me₄NSO₂F was measured in the range of 1–400 hPa (20–120 °C) using a calibrated pressure gauge (MKS).

Dissociation pressure (p (hPa)/ T (°C)): 1.3/20, 2.5/30, 5.4/40, 10.6/50, 19.3/60, 35.0/70, 62.0/80, 106/90, 172/100, 261/110, 400/120.

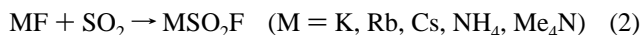
A logarithmic plot of the pressure versus the reciprocal temperature yields a linear correlation (in the range of 20–100 °C) with the equation $\log(p/\text{hPa}) = 10.16 - 2950 \text{ K}/T$.

Attempts to obtain a reliable p/T correlation for NH₄SO₂F failed, since the decomposition was accompanied by sublimation.

Computational Methods. The ab initio calculations for SO₂F⁻ and SOF₂ were performed at the restricted Hartree-Fock level of theory using the Gaussian 94 program.²¹ All calculations were carried out at the 6-31+G* basis level, which augments the standard double- ζ plus polarisation treatment (6-31-G*) with a diffuse set of s,p functions (+) on each heavy atom and is known to describe anionic systems in an appropriate way. Harmonic vibrational frequencies were computed for the minimum-energy structures and scaled by the empirical factor 0.90 to maximize their fit with the experimentally observed frequencies.^{22,23}

Results and Discussion

Synthesis and Properties of Fluorosulfites. The salts of Rb⁺, Cs⁺, NH₄⁺, and Me₄N⁺ are formed in quantitative yields by reacting an excess of SO₂ with the fluorides according to eq 2. In case of KF, only yields of about 85% were obtained.



Quantitative yields of KSO₂F were achieved using KF that was obtained by thermal decomposition of the 85% KSO₂F¹⁸ or using dimethyl sulfoxide as solvent.⁹

The fluorosulfite salts are colorless microcrystalline salts that rapidly decompose on contact with moisture according to eq 3.



The thermal decomposition of the fluorosulfites is more complex. The first step is a simple dissociation in SO₂ and the fluoride. This thermal decomposition is reversible for SO₂

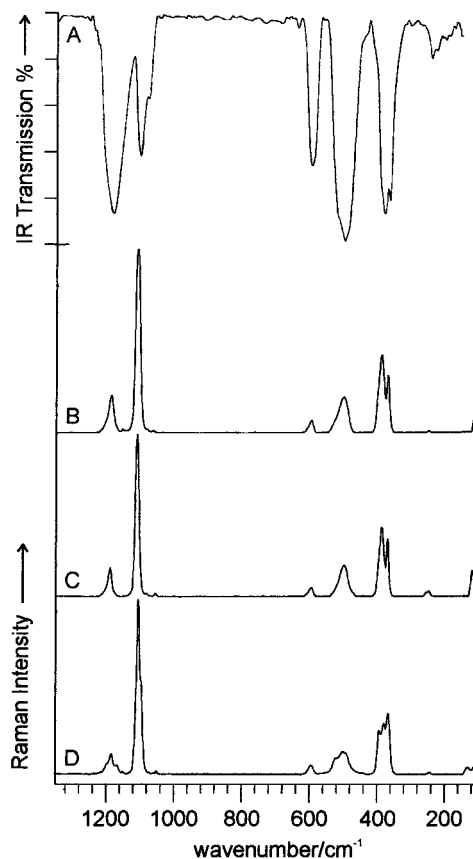
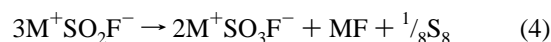


Figure 1. Infrared spectrum of KSO₂F (trace A) and Raman spectra of KSO₂F (trace B), RbSO₂F (trace C), and CsSO₂F (trace D).

pressures up to ca. 200 hPa and can be used to obtain highly reactive fluorides.^{18,24} At higher pressures of SO₂, the salts decompose under formation of the fluorosulfate and sulfur according to eq 4. This disproportionation is accompanied by



the decomposition of Me₄NF, in the case of the Me₄NSO₂F (eq 5). The enthalpy of formation for this salt was derived from



the SO₂ pressure at different temperatures and is discussed later.

The alkali metal and ammonium fluorosulfites are insoluble in nonpolar and polar solvents such as SO₂, CH₃CN, and (CH₃)₂SO. Only Me₄NSO₂F is soluble in SO₂. In acetonitrile, a fast decomposition and evolution of SO₂ were observed. The solution of Me₄NSO₂F in SO₂ strongly tends to oversaturation. Therefore it was not possible to obtain single crystals for X-ray diffraction studies either by slow cooling of the solution or by pumping off the solvent.

Vibrational Spectra. The Raman spectra of KSO₂F, RbSO₂F, and CsSO₂F together with the infrared spectrum of KSO₂F are shown in Figure 1, and the observed frequencies are summarized in Table 1. The vibrational data for NH₄SO₂F and Me₄NSO₂F are listed in Tables 2 and 3, respectively. The assignments for SO₂F⁻ were made by comparison with the isoelectronic ClO₂F (Table 4).²⁵ An ab initio investigation which is discussed later

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Table 1. Vibrational Frequencies (cm^{-1}) of the Alkali Metal Fluorosulfites

KSO ₂ F			RbSO ₂ F			CsSO ₂ F			assignment
IR	IR ^a	Ra	IR	IR ^a	Ra	IR	IR ^a	Ra	
		90 (34)			88 (22)			112 (5)	lattice
		103 (33)			122 (17)			131 (4)	lattice
		248 (1)			247 (3)	239 w		243 (1)	lattice
366 m	270	370 (31)	369 m	265	370 (36)	360 m	275	367 (10)	ν_6 (A'') $\delta_{\text{as}}(\text{OSF})$
381 m	375	388 (42)	379 s	375	387 (43)	380 m	353	378 (12)	} ν_4 (A') $\delta_{\text{s}}(\text{OSF})$
						395 sh		393 (15)	
504 s	495	500 (18)	499 s	497	497 (19)	498 s	485	500 (12)	ν_3 (A') $\delta(\text{OSO})$
596 s		597 (9)	595 s	590	594 (5)	587 m	585	594 (5)	ν_2 (A') $\nu(\text{SF})$
1099 m	1105	1109 (100)	1103 m	1102	1110 (100)	1107 m	1090	1105 (100)	ν_1 (A') $\nu_{\text{s}}(\text{SO})$
						1171 s		1169 (5)	} ν_5 (A'') $\nu_{\text{as}}(\text{SO})$
1179 s	1175	1187 (20)	1183 s	1180	1189 (17)	1186 s	1163	1183 (10)	

^a From ref 6.**Table 2.** Vibrational Frequencies (cm^{-1}) of Tetramethylammonium Fluorosulfite

NMe ₄ ⁺ SO ₂ F ⁻			assignment	
IR	IR ^a	Ra	NMe ₄ ⁺ (<i>T_d</i>)	SO ₂ F ⁻ (<i>C_s</i>)
359 w	260	363 (16)		ν_6 (A'') $\delta_{\text{as}}(\text{OSF})$
383 w	350	383 (7)	ν_8 (E)	ν_4 (A') $\delta_{\text{s}}(\text{OSF})$
456 m		463 (16)	ν_{19} (F ₂)	
498 m	495	494 (2)		ν_3 (A') $\delta(\text{OSO})$
590 m	596	592 (5)		ν_2 (A') $\nu(\text{SF})$
	767	759 (31)	ν_3 (A ₁)	
952 s	950	952 (31)	ν_{18} (F ₂)	
1103 s	1101	1105 (23)		ν_1 (A') $\nu_{\text{s}}(\text{SO})$
1187 s	1187	1196 (4)	ν_7 (E)	ν_5 (A'') $\nu_{\text{as}}(\text{SO})$
		1295 (4)	ν_{17} (F ₂)	
1418 w		1412 (5)	ν_6 (E)	
		1466 (21)	ν_{16} (F ₂)	
1494 s		1474 (44)	ν_2 (A ₁)	
		1487 (4)	ν_{15} (F ₂)	
		2822 (9)		
		2916 (20)		
3029 w		2964 (67)	ν_{14} (F ₂)	
3406 w		3041 (100)	ν_5 (E)	
3468 w				
3550 w				

^a From ref 7.**Table 3.** Vibrational Frequencies (cm^{-1}) of Ammonium Fluorosulfite

NH ₄ ⁺ SO ₂ F ⁻			assignment		
IR	IR ^a	Ra	Ra ^a	NH ₄ ⁺ (<i>T_d</i>)	SO ₂ F ⁻ (<i>C_s</i>)
		110 (14)			
		133 (1)			
		163 (4)			
		200 (8)			
	248	240 (14)	248		
370 w	370	372 (15)	370		ν_6 (A'') $\delta_{\text{s}}(\text{OSF})$
420 m		412 (15)			ν_4 (A') $\delta_{\text{s}}(\text{OSF})$
515 m	483	522 (4)	450		ν_3 (A') $\delta(\text{OSO})$
580 m	580	597 (7)	600		ν_2 (A') $\nu(\text{SF})$
1098 m	1114	1101 (100)	1098		ν_1 (A') $\nu_{\text{s}}(\text{SO})$
1167 s	1167	1168 (6)	1150		ν_5 (A'') $\nu_{\text{as}}(\text{SO})$
		1183 (5)			
1397 vs	1399	1404 (10)	1403	ν_4 (F ₂)	
		1712 (3)		ν_2 (E)	
		1759 (2)		ν_2 (E)	
		3097 (52)	3087	ν_1 (A ₁)	
3094 sh				$\nu_2 + \nu_4$	
3216 s		3184 (29)		ν_3 (F ₂)	

^a From ref 8.

gives, in accordance with the isoelectronic ClO₂F, the expected structure of symmetry *C_s*. Consequently, six fundamentals (4A' + 2A'') which should all be active in both the infrared and the Raman spectra are expected for SO₂F⁻. The assignments of

Table 4. Comparison of Observed and Calculated Frequencies (cm^{-1}) of SO₂F⁻

obsd freq ^a					calcd			assignment
K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺	NMe ₄ ⁺	freq ^b	ClO ₂ F ^c		
368	369	363	371	361	362	367	ν_6 (A'')	$\delta_{\text{as}}(\text{OXF})$
384	383	387	416	383	394	402	ν_4 (A')	$\delta_{\text{s}}(\text{OXF})$
502	498	497	518	496	536	546	ν_3 (A')	$\delta(\text{OXO})$
596	594	590	588	591	605	630	ν_2 (A')	$\nu(\text{SF})$
1104	1106	1108	1100	1104	1086	1106	ν_1 (A')	$\nu_{\text{s}}(\text{XO})$
1183	1186	1184	1167	1191	1174	1271	ν_5 (A'')	$\nu_{\text{as}}(\text{XO})$

^a Average values from infrared and Raman spectra. ^b Scaled by an empirical factor of 0.9. ^c From ref 25.

the Me₄N⁺ and NH₄⁺ cations were made according to well known literature data.^{20,26,27}

The two oxygen–sulfur stretching modes of the SO₂F⁻ anion are observed at 1180 and 1105 cm^{-1} , respectively. The additional bands in this region measured by Robinson et al.⁷ were observed after exposing the sample to moisture and can therefore be attributed to the hydrolysis products according to eq 3.

The sulfur–fluorine stretching mode occurs in the region of 600 cm^{-1} at somewhat lower wavenumbers than for the isoelectronic ClO₂F (630 cm^{-1}). It is remarkably low in comparison to those of the SOF₂ molecule (799 and 737 cm^{-1})²⁸ and indicates a weak sulfur–fluorine bond in agreement with the ab initio calculations.

The three deformation modes are observed in the low-wavenumber region below 600 cm^{-1} . The OSO bending mode occurs at around 500 cm^{-1} . In contrast to previous data,^{6–8} the two OSF bending modes were found close together around 384 and 368 cm^{-1} .

The spectra of KSO₂F and RbSO₂F show similar band shapes for the SO₂F⁻ anion, whereas CsSO₂F exhibits a band splitting for $\nu_{\text{as}}(\text{SO})$ and $\delta_{\text{s}}(\text{OSF})$. The average frequencies for each fluorosulfite salt together with those of the isoelectronic ClO₂F and calculated frequencies are given in Table 4. The observed frequencies for the fluorosulfite salts are almost constant, except for ν_3 , ν_4 , and ν_5 of the NH₄⁺ salt. The deviations are probably due to strong interactions between the anion and the protons of the cation. Overall, the SO₂F⁻ frequencies show the expected trend to appear at somewhat lower wavenumbers than those of the isoelectronic ClO₂F.

Ab Initio Calculation. The ab initio RHF/6-31+G* calculated harmonic frequencies for the SO₂F⁻ anion are given in Table 4 and compared with observed frequencies. We find

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Table 5. Geometry of SO_2F^- (Calculated) Compared to Those of ClO_2F , SOF_2 , and SO_3F^-

	SO_2F^- calc	SOF_2		ClO_2F exp ^b	SO_3F^- exp ^c
		calc	exp ^a		
$r(\text{X}-\text{F})$ (Å)	1.698	1.576	1.583(3)	1.694(3)	1.555(6)
$r(\text{X}-\text{O})$ (Å)	1.458	1.409	1.420(3)	1.420(3)	1.424(4); 1.455(6)
$\angle(\text{O}-\text{X}-\text{O})$ (deg)	113.2			115.2(5)	113.5(2); 117.4(4)
$\angle(\text{O}-\text{X}-\text{F})$ (deg)	100.6	106.6	106.2(2)	101.8(1)	104.5(5); 102.8(3)
$\angle(\text{F}-\text{X}-\text{F})$ (deg)		92.5	92.2(2)		

^a From ref 29. ^b From ref 30. ^c From ref 31.

Table 6. Thermochemical Data of the Fluorosulfites

	dec pt (°C) ^a	ΔH° (kcal/mol)	ΔS° (cal/(mol K))	ΔU (kcal/mol)	$U(\text{MF})$ (kcal/mol)	$U(\text{MSO}_2\text{F})$ (kcal/mol)
KSO_2F	203 ^b	-18.3 ^b	38.4 ^b	25.5	189.7 ^c	164.2
RbSO_2F	267 ^b	-20.8 ^b	38.4 ^b	23.0	181.6 ^c	158.6
CsSO_2F	329 ^b	-23.2 ^b	38.4 ^b	20.6	173.7 ^c	153.1
$\text{Me}_4\text{NSO}_2\text{F}$	139	-14.0	34.1	29.8	159.2	129.4

^a Extrapolated for $p = 1013$ hPa. ^b From ref 6. ^c From ref 35.

reasonable agreement for all vibrational modes. In particular, the ab initio calculations support the experimental result that SO_2F^- frequencies appear throughout at somewhat lower wavenumbers than those of the isoelectronic ClO_2F .

The calculated geometry for SO_2F^- and the isoelectronic SOF_2 are presented in Table 5. For SOF_2 we find an almost perfect agreement with experimental geometries measured by Hargittai et al.²⁹ Therefore, we are confident to predict correct geometries for the SO_2F^- anion. The pyramidal SO_2F^- anion of symmetry C_s has bond angles slightly different from the isoelectronic ClO_2F .³⁰ The S-O bond length of 1.458 Å is somewhat longer than the S-O bond in the isoelectronic SOF_2 and in SO_3F^- ^{29,30} but still in the range of regular sulfur-oxygen double bonds. The obtained S-F bond length of 1.698 Å is remarkably long in comparison to those of SOF_2 and SO_3F^- ³¹ but similar to the weak Cl-F length bond in the isoelectronic ClO_2F . Furthermore the weak S-F bond is in accordance with the thermochemical data of the fluorosulfites.

Enthalpies of Formation. As already discussed, the reaction of fluorides with SO_2 is reversible under certain conditions. Seel et al. derived from the p/T relation the enthalpy (ΔH_f°) and entropy (ΔG_f°) of formation for the KSO_2F , RbSO_2F , and CsSO_2F .⁶ These values and the data obtained by us for $\text{Me}_4\text{NSO}_2\text{F}$ are summarized in Table 6. ΔG_f° for the Me_4N^+ salt is in the range for the alkali metal salts, whereas the ΔH_f° of -14.0 kcal/mol is surprisingly low. We expected a higher value, since Me_4NF is known as the most reactive fluoride in this series and the Me_4N^+ cation is known to stabilize anions like PF_4^- and CO_2F^- ,^{32,33} which are not available as alkali metal salts.

Since the gas phase F^- affinity of SO_2 is known (-43.8 kcal/mol), a rough estimation of the change in lattice energy (ΔU) can be made by eq 6 derived from the Born-Haber cycle,

$$\Delta U = \Delta H_f^\circ + 43.8 \text{ kcal/mol} \quad (6)$$

ignoring differences in heat capacity and polymorphic transitions between 0 and 298 K.³⁴ The ΔU values in Table 6 indicate the largest decrease in lattice energy for $\text{Me}_4\text{NSO}_2\text{F}$. To understand

this apparent contradiction better, a comparison of the lattice energies was made.

Lattice Energy of Me_4NF . The lattice energies (U) are well-known for the alkali metal halides,³⁵ but no data are available on Me_4NF . To derive the lattice energy of Me_4NF , we chose the thermochemical cycle described by Wilson (eq 7).³⁶

$$U = \Delta H_f^\circ(\text{Me}_4\text{N}^+, \text{g}) + \Delta H_f^\circ(\text{F}^-, \text{g}) - \Delta H_f^\circ(\text{Me}_4\text{NF}, \text{c}) + \int_0^{298} \Sigma \Delta H_T + [C_p(\text{Me}_4\text{NF}, \text{c}) - C_p(\text{Me}_4\text{N}^+, \text{g}) - C_p(\text{F}^-, \text{g})] dT \quad (7)$$

The known thermochemical data were used: $\Delta H_f^\circ(\text{Me}_4\text{N}^+, \text{g}) = 129.8$ kcal/mol,³³ $\Delta H_f^\circ(\text{F}^-, \text{g}) = -59.9$ kcal/mol,³⁷ $\Delta H_f^\circ(\text{Me}_4\text{NF}, \text{c}) = -89.0$ kcal/mol.³⁸ The term $\Sigma \Delta H_T$ contains any polymorphic transitions which Me_4NF may undergo between 0 and 298 K. Such transitions are usually of the order 0.25 kcal/mol or less and have been ignored for the calculation.³⁹ The heat capacity term is in the order of 0.28 kcal/mol when the values of $\int_0^{298} C_p dT$ described by Wilson are used.³⁶ The equation yields a lattice energy of 159.2 kcal/mol. Although this calculation incorporates some approximations, it should be more justified than extended-calculation procedures which yield differences for other Me_4N^+ salts in the order of 15 kcal/mol. Such differences are explained by nonionic contributions to the bonding.

The calculated lattice energy of Me_4NF is about 14 kcal/mol smaller than that for CsF . Therefore, reactions with Me_4NF require a lower activation energy and Me_4NF exhibits a higher reactivity than CsF . The fact that the lattice energy decreases more rapidly in the case of the formation of $\text{Me}_4\text{NSO}_2\text{F}$ than for CsSO_2F may be specific for this reaction and cannot be generalized, since thermochemical data are rare in this field.

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