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Gas-Phase Structure, Conformation, and Sulfur 2p Photoelectron Spectroscopy of Pentafluorosulfur Fluorosulfonate, SF_5OSO_2F

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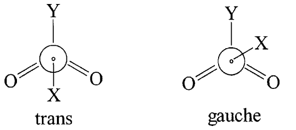
The structure of SF_5OSO_2F has been investigated using gas-phase electron diffraction and quantum-chemical calculations. It is found to exist primarily in the gauche form (SF_5 group gauche relative to the S–F bond of the SO_2F group with ϕ(S–O–S–F = 71(7)°). A small contribution of the trans conformer cannot be excluded. Photoelectron spectroscopy gives ionization energies for the sulfur 2p electrons that reflect the relative electronegativities of fluorine and oxygen. The widths of the peaks in the photoelectron spectra indicate that there is considerable vibrational excitation associated with the core ionization of the sulfur atoms.

Introduction

Sulfonates of the type $XO-SO_2Y$ can adopt different conformations, depending on the torsional orientation of the O−X bond relative to the bonds around sulfur. For steric reasons staggered structures are expected with X either trans or gauche with respect to the S−Y bond (Chart 1). For fluorosulfonates $XO-SO_2F$, different conformational properties have been reported. For the fluorine and chlorine derivatives, $FOSO_2F$ and $ClOSO_2F$, only gauche structures with dihedral angles $\phi(XOSF) \approx 70°$ were observed by gas electron diffraction (GED).[1] Ab initio calculations (HF/6-31G*) predict a second minimum in the torsional potentials of these compounds at $\phi(XOSF) = 180°$ (trans conformation).[1] Its energy is higher than that for the gauche form by 2.8 kcal/mol ($FOSO_2F$) and 2.1 kcal/mol ($ClOSO_2F$). Similar relative energies are predicted also by the hybrid method B3LYP/6-31G* (see below). Microwave spectra of CH_3OSO_2F were interpreted in terms of a trans conformation.[2] GED intensities of this compound are not sensitive toward the conformational properties, but make the presence of an additional gauche conformer very likely. According to quantum chemical calculations the potential function to internal rotation around the S−O bond possesses minima only for gauche structures and the trans form corresponds to a transition state (see below).

Chart 1



In the present study we report a structural and conformational investigation of SF_5OSO_2F, based on GED and quantum chemical calculations. The conformational properties of this compound are of interest in comparison with the previously studied fluorosulfonates, since the SF_5 group is a very bulky substituent. Furthermore, the geometric parameters of the S−O−S skeleton are interesting in context with those of the two symmetrically substituted compounds $FO_2S-O-SO_2F$[3] and $F_5S-O-SF_5$.[4] In addition to obtaining structural information we have also measured the sulfur 2p photoelectron spectra of SF_5OSO_2F and SF_6. The ionization energies provide insight into the electronic structure of the molecules, while the spectral shapes give information on the

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changes in molecular shape that accompany photoionization.

The first synthesis of SF_5OSO_2F involved the photochemical reaction of SO_2 with SF_5Z (Z = Cl, SF_5, SF_5OO).[5] In the same year, it was reported that the reaction of F_2 with sulfur produced SF_5OSO_2F (the fluorine was contaminated with oxygen or OF_2).[6] Additional pathways include the reaction of SF_5OF with SO_2 and the thermal reaction of SF_5OOSF_5 with SO_2.[7,8] More recently, SF_5OSO_2F was prepared in high yield and purity from SF_5Br and $BrSO_3F$.[9] SF_5OSO_2F is a decomposition product in electric discharges of the gaseous insulator SF_6 in the presence of oxygen or water.[10] The vibrational spectra of this compound have been reported.[11] SF_5OSO_2F is a colorless liquid, with a boiling point of 39.6 °C,a density of 1.867 g/mL, and Trouton constant of 22.1.

Quantum Chemical Calculations

All quantum chemical calculations were performed with the GAUSSIAN98 program package,[12] using primarily the 6-31G* basis set and both B3LYP and MP2 methods. Some calculations have been made using the cc-pVTZ basis sets. Core ionized molecules have been simulated using the equivalent-cores approximation. That is, the core ionized sulfur has been replaced by a chlorine cation and the calculation has been performed for the singly charged molecular ion.

Structure optimizations were performed for fixed torsional angles ϕ(SOSF) in steps of 30° with both MP2 and B3LYP methods. Both functions are very similar, and only the result derived with the B3LYP method is shown in Figure 1. This curve possesses minima for gauche and trans conformations with the gauche form being lower in energy. The relative energy of the trans form is 1.03 (B3LYP) and 1.11 kcal/mol (MP2), respectively, and the relative Gibbs free energy is 1.95 and 2.11 kcal/mol, if the different multiplicities for gauche ($m = 2$) and trans conformers ($m = 1$) are taken into account. It should be pointed out that the SF_5 group staggers the $O-SO_2F$ bond in the gauche conformer, but it eclipses this bond in the trans form. Vibrational amplitudes and vibrational corrections for interatomic distances were derived from a calculated (B3LYP) force field using the method of Sipachev and the program SHRINK, which takes the nonlinear relation between Cartesian and internal coordinates into account.[13] The application of such vibrational corrections transforms r_a to r_{h1} distances.

Core-ionization energies can be obtained as the difference between the energy of the neutral molecule and that of the ionized molecule. The equivalent cores approximation does not, however, give the energy of the ionized molecule, but an energy that differs from this by the amount involved in exchanging a chlorine cation for a core-ionized sulfur atom. We expect this energy to be approximately independent of species, with the result that the difference will cancel out if we calculate *relative* ionization energies. We have used this approach to obtain sulfur 2p ionization energies relative to that in SF_6.

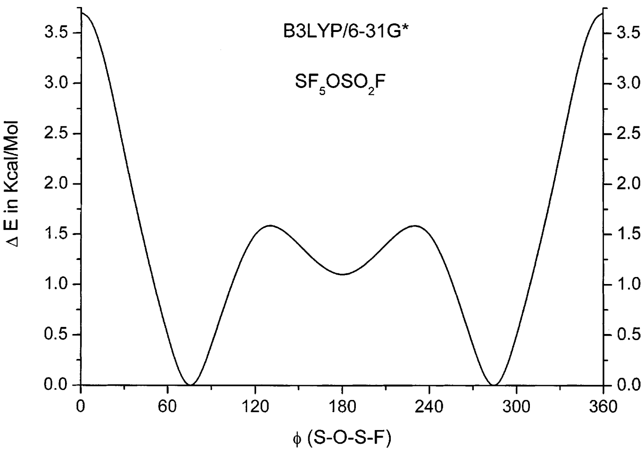

Figure 1. Calculated potential function for internal rotation around S1−O1 bond.

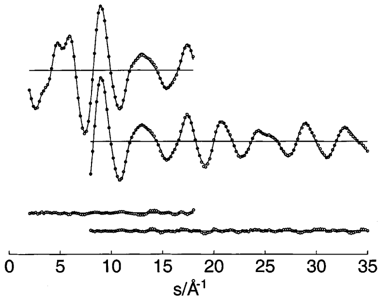

Figure 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Experimental Section

SF_5OSO_2F was prepared from $BrSO_3F$ and SF_5Br as described by Johri, Katsuhara, and DesMarteau.[9] Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[14] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to −35 °C, and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with an Agfa Duoscan HiD scanner, and total scattering intensity curves were obtained from the TIFF file using the program SCAN3.[15] Experimental molecular intensities (Figure 2) were obtained in the range $s = 2-18$ and $8-35$ Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} for the long and short camera distances, respectively, ($s = (4\pi/\lambda)(\sin \theta/2)$, where λ is the electron wavelength and θ is the scattering angle).

Sulfur 2p photoelectron spectra of SF_6 and SF_5OSO_2F were measured at the MAX-lab using beamline I411[16] at a photon energy

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of 220 eV. The photoelectrons were detected and analyzed in a Scienta SES 200 analyzer. The combined monochromator and analyzer slits and the analyzer pass energy were chosen to give a resolution of about 40 meV in the photoelectron spectra.

The spectra have been fit by least squares with peak shapes that include the effects of resolution, lifetime, and the interaction of the photo and Auger electrons (postcollision interaction, or PCI). The line shape given by eq 12 from van der Straten et al.[17] was used to describe the effect of PCI. This was convoluted with a Gaussian function, which in the case of SF_6 represents the effect of the experimental resolution and in the case of SF_5OSO_2F represents the combined effect of the experimental resolution and the vibrational (or dissociative) broadening. For SF_6, four peaks have been used in the fitting. These are to take into account transitions to the ground vibrational state of the molecule (adiabatic transition) and to the $v = 1$ excitation of the sulfur−fluorine symmetric stretching mode. Also included in the fits is a constant background.

For SF_6, the Lorentzian lifetime width and the Gaussian experimental resolution are treated as fitting parameters. The value for the resolution that was obtained is 45 meV, in keeping with the value of about 40 meV expected from the choice of instrumental parameters. The Lorentzian width is 47 meV. The $v = 1$ vibrational excitation is found to be at an energy of 92 meV. The vertical ionization energy (that is, the average over the spectrum) for SF_6 has been reported to be 180.21 ± 0.05 eV.[18] Taking this, together with the spin−orbit splitting of 1.21 eV and a 2:1 ratio for the intensities of the spin−orbit components, we can infer an ionization energy of the adiabatic peak of 180.20 eV, which is in good agreement with the value reported by others.[19,20] This value provides the calibration for the ionization-energy scale.

For SF_5OSO_2F we have used the same lifetime width as was found for SF_6. As noted, the combined effect of instrumental broadening and vibrational broadening has been described using a Gaussian shape. The two peaks comprising the spin−orbit doublets are constrained to have the same Gaussian width, but this parameter is allowed to be different for the two different kinds of sulfur in this molecule.

Structure Analysis

The radial distribution function (Figure 3) which was obtained by Fourier transformation of the molecular intensities is reproduced satisfactorily only with a gauche conformation, in agreement with quantum chemical calculations. The molecule contains some closely spaced bond lengths and one-angle nonbonded interatomic distances, which cannot be resolved individually in a gas-phase electron diffraction analysis. For such parameters, mean values were derived in the experiment, and differences between these bond lengths or bond angles were constrained to calculated values. This applies to the difference between S1−O1 and S2−O1, between S1−F1 and S2−F distances, and between the O1−S=O2 and O1−S=O3 bond angles. If the two computational methods, B3LYP and MP2, predict slightly different values for some differences, mean values were used (see Table 1). If the predicted difference between geometric parameters is smaller than the experimental uncertainty for the mean value, these parameters were set equal. This applies to the two S=O bond lengths and the F1−S1=O bond angles in the SO_2F group and to the $S-F_{eq}$ bond lengths and $F_{ax}-S-F_{eq}$ bond angles in the SF_5 group. The B3LYP method predicts the $S-F_{ax}$ bond (S2−F2 in Figure 4) of the SF_5 group slightly shorter than the equatorial bonds $S-F_{eq}$ (S2−F3 to S−F6) and the MP2 approximation slightly longer. Therefore, all S−F bonds in the SF_5 group were set equal in the structure analysis. Thus, C_{4v} symmetry was assumed for

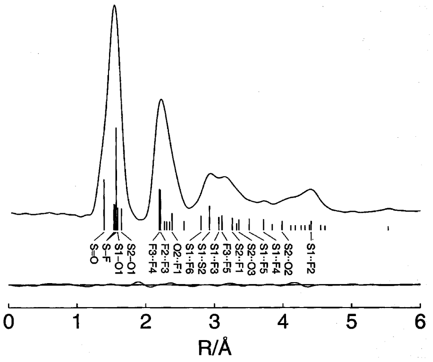

Figure 3. Experimental radial distribution function and difference curve RDF(exp) − RDF(calc). Important interatomic distances are indicated by vertical bars.

Table 1. Experimental and Calculated Geometric Parameters of SF_5OSO_2F

	GED[a]		B3LYP/6-31G*[b]	MP2/6-31G*[b]
S1−O1	1.599(9)	p1	1.651	1.652
S2−O1	1.654(9)[c]		1.715	1.698
S=O	1.400(3)	p2	1.436	1.436
S2−F	1.555(2)	p3	1.601	1.597
S1−F1	1.550(2)[d]		1.594	1.593
S1−O1−S2	129.1(13)	p4	126.4	125.8
O1−S1=O2	105.4(12)	p5	103.2	103.0
O1−S1=O3	114.4(12)[e]		112.3	112.0
F1−S1−O1	96.8(25)	p6	97.8	97.4
F1−S1=O	108.0(21)	p7	107.6	107.5
$F_{eq}-S2-F_{ax}$	91.4(6)	p8	90.2	90.1
tilt(SF_5)[f]	4.6(10)	p9	2.9	2.9
ϕ(S2−O1−S1−F1)	71(7)	p10	76.1	75.4
ϕ(S2−O1−S1=O3)	−40(7)		−36.5	−36.9
ϕ(S1−O1−S2−F3)	64(3)	p11	62.7	64.7
ϕ(S1−O1−S2−F6)	−26(3)		−27.2	−25.3

[a] r_{h1} values in Å and deg with 3σ uncertainties. For atom numbering see Figure 4. [b] Mean values for parameters which are not unique. [c] (S1−O1) − (S2−O1) fixed to 0.055[10] Å. The estimated uncertainty in brackets is taken into account in the uncertainties of the individual bond lengths. [d] (S2−F) − (S1−F1) fixed to 0.005 Å. [e] (O1−S1=O3) − (O1−S1=O2) fixed to 9°. [f] Tilt angle of the SF_5 group, see text.

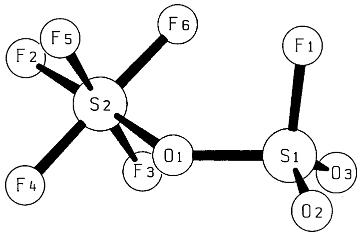

Figure 4. Molecular model with atom numbering.

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Table 2. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes[a]

	distance	ampl (GED)		ampl (MP2)
S=O	1.40	0.035[b]		0.035
S−F	1.55−1.56	0.042(2)	*l*1	0.042
S−O	1.60−1.65	0.051[b]		0.051
F···F	2.20−2.23	0.059(5)	*l*2	0.068
O1···F	2.21−2.28	0.077[b]		0.077
O1···F1	2.35	0.075[b]		0.075
F1···O2	2.39	0.065[b]		0.065
O1···O	2.39−2.52	0.068[b]		0.068
O2···O3	2.44	0.051(9)	*l*3	0.056
F1···F6	2.55	0.202[b]		0.202
S1···F6	2.80	0.115(21)	*l*4	0.125
O3···F3	2.83	0.220[b]		0.220
S1···S2	2.93	0.051(9)	*l*3	0.056
O3···F6	2.97	0.218[b]		0.218
S1···F3	3.03	0.144[b]		0.144
F3···F5	3.11	0.056(18)	*l*5	0.054
O1···F2	3.20	0.056(18)	*l*5	0. 060
S2···F1	3.26	0.115(21)	*l*4	0.131
F1···F5	3.34	0.263[b]		0.263
S2···O3	3.35	0.075(19)	*l*6	0.111
S1···F5	3.51	0.115(21)	*l*4	0.131
S1···F4	3.72	0.075(19)	*l*6	0.096
F1···F3	3.80	0.166[b]		0.166
S2···O2	3.98	0.070[b]		0.070
O2···F6	4.10	0.115(21)	*l*4	0.119
O2···F3	4.14	0.161[b]		0.161
O3···F4	4.25	0.150[b]		0.150
O2···F5	4.32	0.144[b]		0.144
S1···F2	4.39	0.079[b]		0.079
F1···F4	4.40	0.115(21)	*l*4	0.125
O2···F4	4.40	0.129[b]		0.129
F1···F2	4.52	0.177[b]		0.177
O3···F2	4.56	0.161[b]		0.161
O2···F2	5.52	0.078[b]		0.078

[a] Values in Å with 3σ uncertainties. For atom numbering see Figure 4. [b] Not refined.

the SF_5 group with a possible tilt angle between the C_4 axis and the O1−S2 bond direction. This tilt occurs in the S1−O1−S2 plane away from S1. Vibrational amplitudes were collected in groups according to calculated values. Amplitudes that caused large correlations with geometric parameters and amplitudes that were poorly determined in the gas-phase electron diffraction experiment were not refined. With these constraints eleven r_{h1} geometric parameters, p1 to p11, and six vibrational amplitudes, *l*1 to *l*6, were refined simultaneously. The following correlation coefficients had values larger than |0.6|: p1/p4 = −0.79, p6/p7 = −0.68, p6/p11 = 0.74, p7/p11 = −0.63 and p1/*l*1 = −0.75. The results are listed together with calculated values in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes), and the molecular model is shown in Figure 4.

Additional least squares refinements were performed for mixtures of gauche and trans conformers. The geometric parameters of the trans form were tied to those of the gauche conformer using the calculated differences, and calculated amplitudes were used. The agreement factor remained unchanged for contributions of less than 10% of the trans form and increased for larger contributions.

Discussion of the Structure

Only the gauche conformer of SF_5OSO_2F is observed in the gas-phase electron diffraction experiment, but a small contribution of the trans form (<10%) cannot be excluded. This result is in agreement with the quantum chemical calculations, which predict a trans contribution of about 4%. Thus, the conformational properties of this compound are the same as those of $FOSO_2F$ and $ClOSO_2F$, for which also only the gauche form was observed experimentally. Calculated (B3LYP) potential curves for internal rotation around the S−O bond in these three compounds are very similar with minima at gauche and trans orientation and the gauche conformation favored (Figure 5). As mentioned in the Introduction, the experimentally determined conformational properties of CH_3OSO_2F are different. For this fluorosulfonate a microwave and GED investigation resulted in a trans conformer with some contribution of the gauche form. However, the calculated (B3LYP) potential curve for this compound, which is also shown in Figure 5, possesses minima only for the gauche form and a flat maximum in the trans region (ϕ(X−S−O−F) = 180°), about 1.8 kcal/mol higher in energy. An additional calculation with the MP2/cc-pVTZ method (not shown in Figure 5) predicts an additional shallow minimum for the trans structure, 2.3 kcal/mol higher in energy than the gauche form. These calculated potential functions are not compatible with the experimental results.

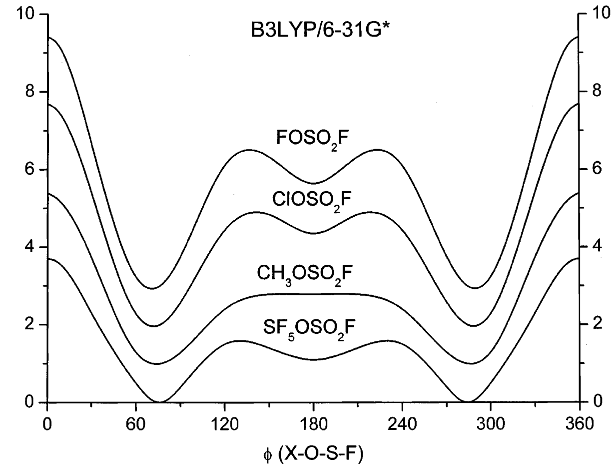

Figure 5. Calculated (B3LYP/6-31G*) potential functions for internal rotation in fluorosulfonates $XOSO_2F$. Each curve is shifted by 1 kcal/mol.

The dihedral angles around the S1−O1 bond in SF_5OSO_2F (ϕ(S2−O1−S1−F1) = 71(7)° and ϕ(S2−O1−S1=O3) = −40(7)°) imply that the SF_5 group is rotated closer to the S=O double bond than to the S1−F1 single bond, which contradicts chemical intuition. On the other hand, the nonbonded distance S2···F1 (3.26 Å) is shorter than the S2···O3 contact (3.35 Å). The ϕ(S2−O1−S1−F1) dihedral angle is equal to the X−O−S−F dihedral angle in $FOSO_2F$ and $ClOSO_2F$ within their experimental uncertainties. Geometric parameters of the SO_2F group in the four fluorosulfonates $XOSO_2F$ with X = F, Cl, CH_3, and SF_5 are almost equal within their experimental uncertainties. The S−O single bond decreases with decreasing electronegativity of the substituent X from 1.606(8) Å in $FOSO_2F$ to 1.558(7) Å in CH_3OSO_2F. This bond length is intermediate in the chlorine (1.585(10) Å) and SF_5 derivatives (1.599(9) Å). This trend can be rationalized qualitatively by a simple electrostatic

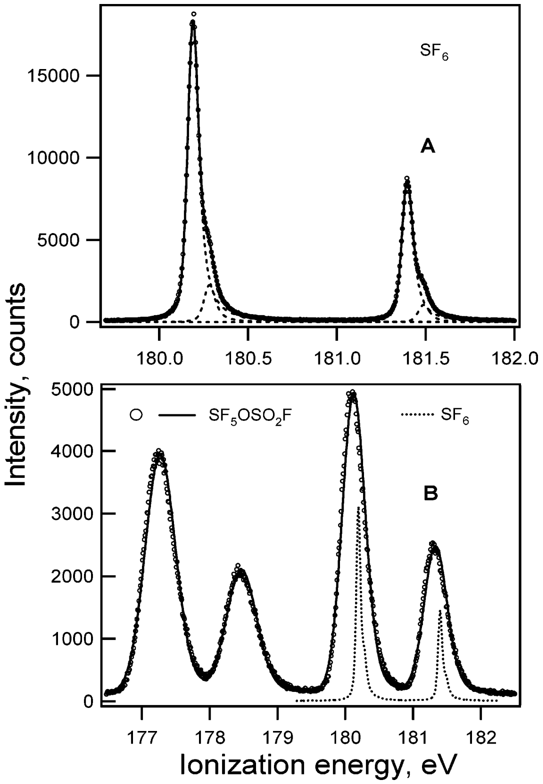

Figure 6. Sulfur 2p photoelectron spectra of SF_6 and SF_5OSO_2F. Open circles show the experimental data. Solid lines show least-squares fits to the data. Dashed lines show individual components of the fit for SF_6.

model. The oxygen net charge becomes more negative with decreasing electronegativity of X, and thus the electrostatic attraction between oxygen and the highly positive sulfur atom increases. SF_5OSO_2F contains two types of S(VI)−O bonds, $FO_2S{-}O$ (1.599(9) Å) and $F_5S{-}O$ (1.654(9) Å), which differ by 0.055[10] Å. This difference was not refined in the gas-phase electron diffraction analysis; it was fixed to a mean value of the two quantum chemical methods (0.064 Å from B3LYP and 0.046 Å from MP2). Within experimental error limits, the $FO_2S{-}O$ bond length is equal to that in the symmetrically substituted disulfuryl fluoride, $FO_2S{-}O{-}SO_2F$ (1.611(10) Å).[3] The $F_5S{-}O$ bond in SF_5OSO_2F, however, is appreciably longer than that in $F_5S{-}O{-}SF_5$ (1.586(11) Å).[4] This can be rationalized with the much larger O−S−O angle in the latter compound (142.5(16)°).

Both quantum chemical methods predict all bond distances in this compound too long by up to 0.06 Å. The experimental bond angles are reproduced to within ±3° and dihedral angles to within their experimental uncertainties.

The Photoelectron Spectrum

The experimental sulfur 2p photoelectron spectra for SF_5OSO_2F and SF_6 are shown in Figure 6, where the data are represented by open circles and least-squares fits to the data are represented by solid lines. For each sulfur atom the 2p spectrum has two components, $2p_{1/2}$ and $2p_{3/2}$, with an intensity ratio of about 2:1. For the SF_6 spectrum (Figure 6A) additional structure is apparent, and this is due to excitation of the sulfur−fluorine symmetric stretching vibrational mode. For SF_5OSO_2F (Figure 6B) the peaks are broad and featureless, indicating either a high degree of vibrational broadening or that the core-ionized state is dissociative. In Figure 6B the SF_6 spectrum is shown for comparison as a dashed line.

Table 3. Sulfur 2p Ionization Energies, eV

			ΔI $2p_{3/2}$		
	$2p_{3/2}$	$2p_{1/2}$	expt	theor	ref
SF_6	180.20	181.41	0	0	*a*
$S^*F_5OSO_2F$	180.09	181.30	−0.11	−0.42	*b*
$SF_5OS^*O_2F$	177.23	178.42	−2.97	−3.03	*b*
SF_4	177.8		−2.4	−3.62	*c*
SO_2F_2	177.67		−2.53	−2.31	11

[a] References 18, 19, 20 for $2p_{3/2}$. This work for spin−orbit splitting to give $2p_{1/2}$. [b] This work. [c] Using average 2p ionization energy of 178.2 eV from ref 21, together with assumed spin−orbit splitting of 1.2 eV and spin−orbit intensity ratio of 2:1.

Ionization Energies. The experimentally determined vertical ionization energies are listed in Table 3. Also given here are the sulfur 2p ionization energies of SF_4[21] and SO_2F_2[22] for comparison. The values are listed both as absolute values and as values for the $2p_{3/2}$ ionization energy relative to that in SF_6. The ionization energies are consistent with the relative electronegativities of fluorine and oxygen. One of the sulfur atoms in SF_5OSO_2F is 6-fold coordinated as is the sulfur atom in SF_6. We are thus comparing SF_5O with SF_6, and the sulfur ionization energy is slightly lower in the former than the latter, reflecting the lower electronegativity of oxygen. The other sulfur atom in SF_5OSO_2F is 4-fold coordinated as are SF_4 and SO_2F_2. With three oxygen atoms and one fluorine atom, its ionization energy is lower than that in either of the other two molecules, which have more fluorine atoms and fewer oxygen atoms. Also shown in the table are the calculated relative ionization energies. Except for the value for SF_4, these approximately reproduce the experimental results. Since calculations at several different levels give similar results, we suspect that there may be an error in the reported experimental value.

For the compound SF_5OSO_2F, the sulfur ionization energy in the SF_5 group is almost as high as that of the sulfur in SF_6 and is considerably higher than that of sulfur in several SF_5X compounds (X = Br, SF_5, Cl, CF_3).[18] This high ionization energy reflects the high electronegativity of the fluorosulfonate group. True et al.[18] used a correlation between electronegativity of the halogens and the sulfur ionization energy to estimate the electronegativities of the CF_3 and SF_5 groups. Applying the same approach to the fluorosulfonate group, we can conclude that this group has an electronegativity similar to that of fluorine.

Vibrational Structure. The analysis of the SF_6 photoelectron spectrum shows that the $v = 1$ excitation of the A_{1g} symmetric stretching mode comes at an energy of 0.092 eV (744 cm^{-1}). This is in approximate agreement with the harmonic frequency calculated for the equivalent-cores species, ClF_6^+, of 663 cm^{-1} (B3LYP/6-31G**), 692 cm^{-1}

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(MP2/6-31G**), or 726 cm^{-1} (MP2/cc-pVTZ). The intensity of the $v = 1$ excitation is 12.3% of that of the $v = 0$ transition. Using the harmonic oscillator model to calculate Franck−Condon factors, we find that this intensity ratio implies a change in equilibrium sulfur−fluorine bond length of ±1.0 pm upon ionization. The theoretical calculations using the MP2/cc-pVTZ method indicate that this bond decreases in length by −0.41 pm, but other calculations indicate an increase in bond length upon core ionization. In all cases, the bond-length change is small, and in this sense, SF_6 is similar to CF_4, which also shows a very small change upon ionization.[23] For SF_5OSO_2F, the peaks in the photoelectron spectra are broad, indicating a high degree of vibrational excitation, or, possibly, that the core-ionized molecule is dissociative. The widths of the peaks corresponding to ionization of the OSO_2F group (0.53 eV) are noticeably greater than those for the SF_5O group (0.40 eV). Comparing the geometries of the neutral and core-ionized molecules, we find that the major change of equilibrium bond lengths is in the oxygen sulfur bond for the sulfur that has not been core ionized. For ionization of the sulfur in OSO_2F, the $SF_5{-}O$ bond length increases by 38 pm, and for ionization of the sulfur in SF_5O, the $O{-}SO_2F$ bond length increases by 17 pm. There is, therefore, much more vibrational excitation associated with ionization of the OSO_2F sulfur than with ionization of the SF_5O sulfur, and this excitation is reflected in the widths of the peaks. The calculations indicate that ionization of the OSO_2F sulfur leads to a vibrational excitation of about 0.5 eV, while ionization of the SF_5O sulfur leads to an excitation of only about 0.3 eV. These energies are very similar to the observed Gaussian widths of the peaks in the spectrum, 0.50 and 0.37 eV, respectively, which should reflect this excitation energy.

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