SUPPORTING INFORMATION

Synthesis and Characterization of SF_4 Adducts with Polycyclic Amines

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Table S1. Crystal Data Collection Parameters and Results of $C_6H_{12}N_2{\cdot}2SF_4$ and $C_6H_{12}N_4{\cdot}2SF_4$.

Compound	$C_6H_{12}N_2{\cdot}2SF_4$	$C_6H_{12}N_4{\cdot}2SF_4$
Empirical Formula	$C_6H_{12}F_8N_2S_2$	$C_6H_{12}F_8N_4S_2$
Formula weight, g mol^{-1}	328.30	356.32
Temperature, K	153	153
Wavelength, Å	0.71073	0.71073
Crystal System	Monoclinic	Orthorhombic
Space Group	*P*2$_1$/*c*	*Pnma*
Unit Cell	a = 13.87(2) Å b = 7.859(14) Å c = 11.33(2) Å β = 101.572(19)°	a = 28.96(4) Å b = 7.081(9) Å c = 6.113(7) Å
Volume, Å^3	1210(4)	1254(3)
Z	4	4
μ (mm^{-1})	0.53	0.52
Density (calc.), g cm^{-1}	1.802	1.888
F(000)	664	720
Crystal Size, mm^3	0.33 × 0.12 × 0.09	0.26 × 0.16 × 0.07
Reflections Collected	12237	10477
Independent Reflections	2753	1565
Data/Restraints/ Parameters	2753/0/163	1565/0/124
Goodness-of-fit on F^2	1.13	1.13
$\Delta\rho_{max}$ (e Å^{-3})	0.38	0.38
$\Delta\rho_{min}$ (e Å^{-3})	−0.43	−0.35
$R_{1,}$ $I > 2\sigma(I)$ [a]	0.0469	0.0319
wR_2 (F^2) [a]	0.0832	0.0759
CCDC	1994897	1994893

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - Fc^2)^2/ \Sigma w(F_o^4)]^{1/2}$.

Table S2. Crystal Data Collection Parameters and Results of $[C_6H_{12}N_2H]_2F[SF_5]\cdot 6SF_4$, $[C_6H_{12}N_4H][HF_2]\cdot SF_4$, $[C_6H_{12}N_4H][H_2F_3]\cdot HF$, and $[C_7H_{13}NH]F\cdot 3.5SF_4$.

Compound	$[C_6H_{12}N_2H]_2F[SF_5]\cdot 6SF_4$	$[C_6H_{12}N_4H][HF_2]\cdot SF_4$	$[C_6H_{12}N_4H][H_2F_3]\cdot HF$	$[C_7H_{13}NH]F\cdot 3.5SF_4$
Empirical Formula	$C_{12}H_{26}F_{30}N_4S_7$	$C_6H_{14}F_6N_4S$	$C_6H_{16}F_4N_4$	$C_7H_{14}F_{15}NS_{3.5}$
Formula weight, g mol^{-1}	1020.79	288.27	220.23	509.40
Temperature, K	163	143	153	153
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Orthorhombic	Monoclinic	Trigonal
Space Group	*Pbca*	*Pnma*	$P2_1/c$	*R-3c*
Unit Cell	a = 22.75(5) Å b = 12.51(3) Å c = 25.65(5) Å	a = 26.774(4) Å b = 6.9798(10) Å c = 5.9194(9) Å	*a* = 6.2294(8) Å *b* = 11.3779(15) Å *c* = 13.5652(18) Å *β* = 98.6650(17)°	a = 10.9546(19) Å b = 10.9546(19) Å c = 52.812(18) Å
Volume, Å^3	7300(25)	1106.2(3)	950.5(2)	5489(3)
Z	8	4	4	12
μ (mm^{-1})	0.60	0.36	0.15	0.60
Density (calc.), g cm^{-1}	1.858	1.731	1.539	1.849
F(000)	4064	592	464	3048
Crystal Size, mm^3	0.35 × 0.20 × 0.10	0.10 × 0.05 × 0.01	0.30 × 0.02 × 0.01	0.20 × 0.15 × 0.04
Reflections Collected	77262	8384	12625	24641
Independent Reflections	8007	1228	1947	1432
Data/Restraints/ Parameters	8007/22/501	1228/43/101	1947/0/139	1432/0/84
Goodness-of-fit on F^2	1.04	1.14	1.04	1.02
$\Delta\rho_{max}$ (e Å^{-3})	0.85	0.50	0.24	1.01
$\Delta\rho_{min}$ (e Å^{-3})	−0.67	−0.39	−0.22	−0.44
R_1, $I > 2\sigma(I)$ [a]	0.0670	0.0500	0.0394	0.0442
wR_2 (F^2) [a]	0.1717	0.1102	0.0901	0.1175
CCDC	1994898	1994894	1994896	1994895

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - Fc^2)^2/ \Sigma w(F_o^4)]^{1/2}$.

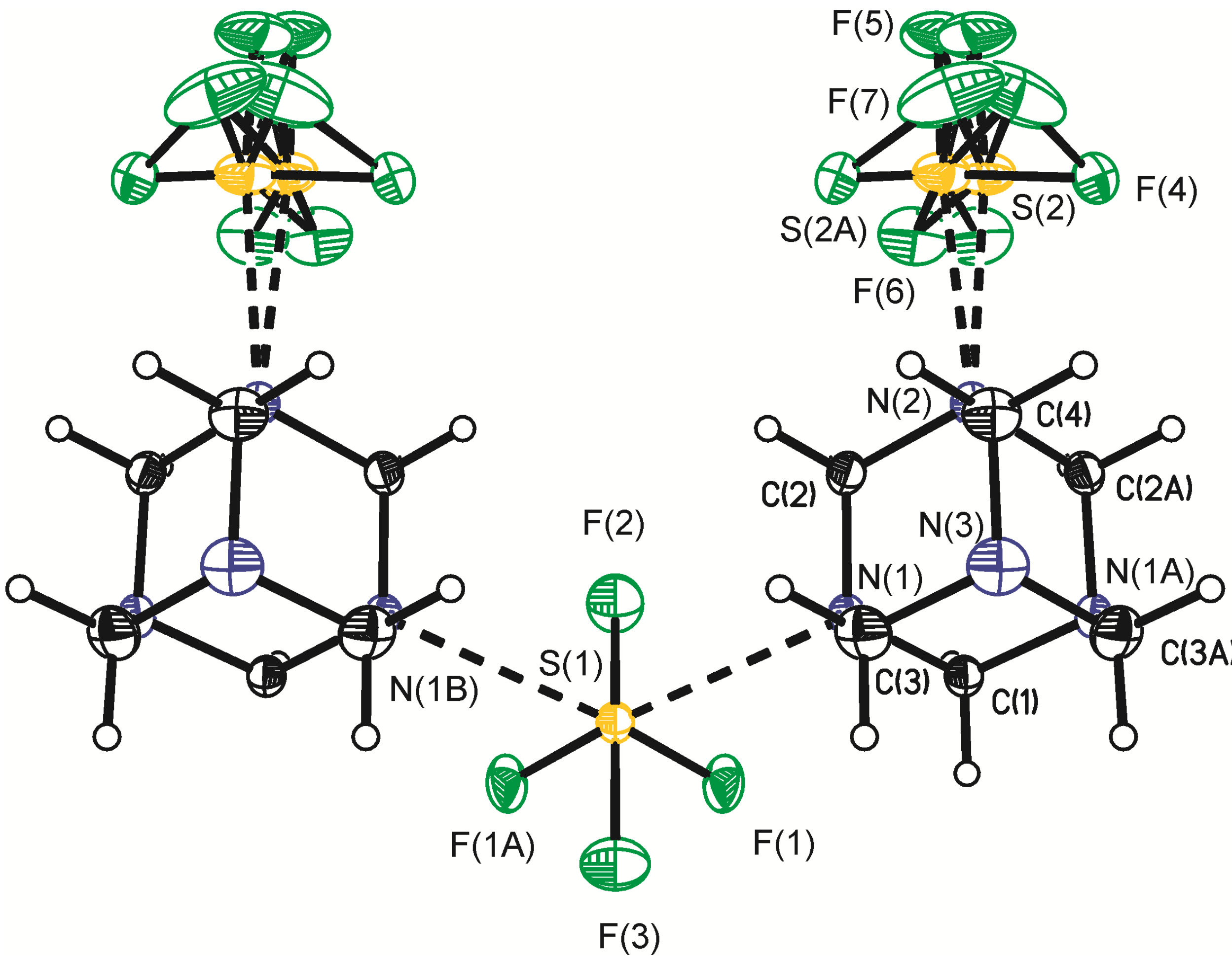

Figure S1. Thermal ellipsoid plot of $C_6H_{12}N_4{\cdot}2SF_4$. Thermal ellipsoids are depicted at the 50% probability level.

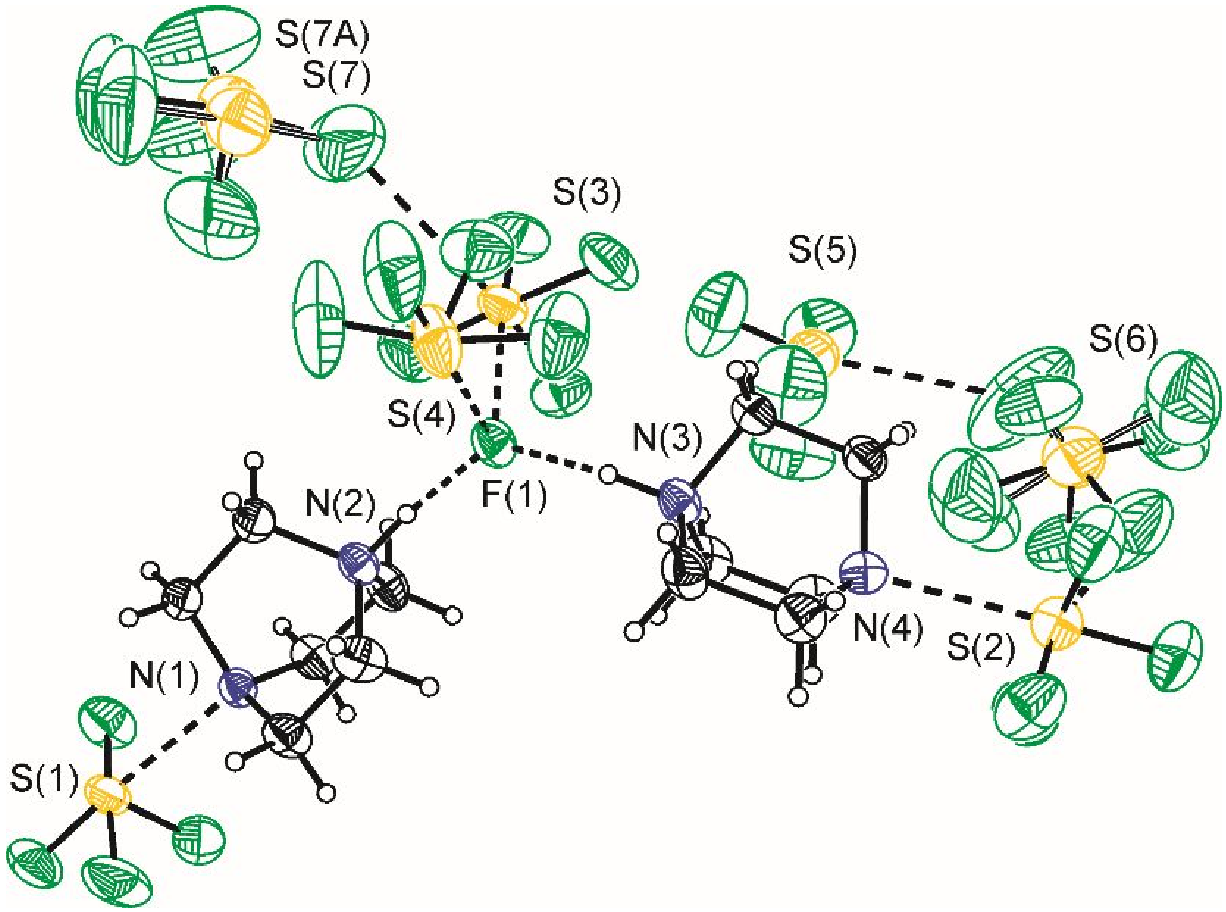

Figure S2. Thermal ellipsoid plot of $[C_6H_{12}N_2H]_2F[SF_5]\cdot 6SF_4$. Thermal ellipsoids are depicted at the 50% probability level.

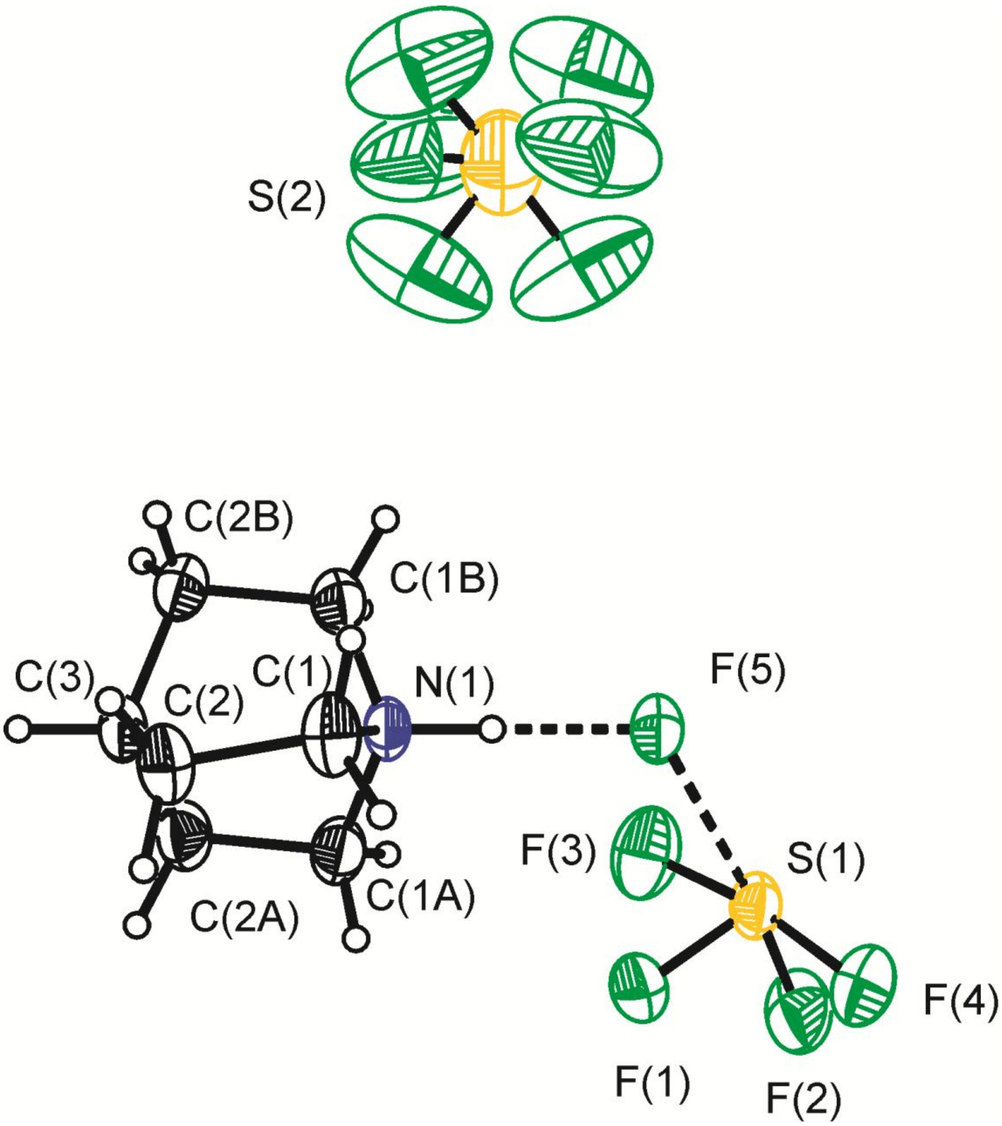

Figure S3. Thermal ellipsoid plot of the $C_7H_{13}NH$---F---$SF_4 \cdot SF_4$ moiety in $[C_7H_{13}NH]^+$ $F^- \cdot 3.5SF_4$. Thermal ellipsoids are depicted at the 50% probability level.

Table S3. Observed and Calculated Frequencies for SF_4, $C_6H_{12}N_2$, $C_6H_{12}N_2{\cdot}2SF_4$, and $[C_6H_{12}N_2H]^+{}_2F^-[SF_5]^-{\cdot}6SF_4$. Bands Associated with the SF_4 Moiety are Highlighted.

SF_4			$C_6H_{12}N_2$	$C_6H_{12}N_2{\cdot}2SF_4$	$[C_6H_{12}N_2H]^+{}_2F^-[SF_5]^-{\cdot}6SF_4$	
exptl[a]	calcd[a,d]	assignments[a,b]	exptl[c]	exptl[d]	exptl[e]	assignments[b]
			3001(3)	3003(19)	3029(32)	
			2945(81)	2977(26)	3019(33)	
			2938(82)	2951(20)	2998(69)	
			2924(82)	2941sh	2972(54)	$\nu(CH_2)$ + overtones and
			2901(17)	2909sh	2951sh	combination modes
					2923sh	
			2870(100)	2895(9)	2906(19)	
			2713(1)			
			2639(3)			
			2625(2)	2629(1)		Overtones or combination modes
			2614(2)			
			2589(3)			
				1482(8)	1508(20)	
			1457(44)	1465(20)	1466(53)	$\delta(CH_2)$
			1444sh	1451sh		
			1346(7)	1354(74)	1392(15)	$\nu(CH_2)/\nu(CC)$
			1325(15)	1331(6)	1374sh	$\omega(CH_2)$
			1299(36)	1304(9)[f]	1292(24)	$\tau(CH_2)$
					1071sh	
			1060(28)	1062(17)	1063(63)	$\nu_{as}(NC_3)$
				1024(3)	1033(12)	
					1008(39)	
			971(61)	990(100)	992(73)	$\nu(CC)/\omega(CH_2)$
					986sh	
			918(2)	929(2)	911(19)	$\nu(CC)$
			894(5)	911(2)		
892	856(13)[102]	$\nu_s(SF_{2,eq})$			884(85)	SF_4, $\nu_s(SF_{2,eq})$
					879sh	SF_4, $\nu_{as}(SF_{2,eq})$
				836(43) 821(53)	845sh 836(85)	N---SF_4, $\nu(SF_{apical})$
			829(1)	826sh	827sh	$\rho(CH_2)$

						806(67) 799sh		811sh 795(33) 786(42) 779sh		813(69) 808sh		$\nu_s(NC_3)$
										795(31)		SF_5^-, $\nu(SF_{apical})$
867		825(4)[170]		$\nu_{as}(SF_{2,eq})$				728(71)[f]		766sh 751(80)		N---SF_4, $\nu(SF_{trans})$
730		703(<1)[630]		$\nu_{as}(SF_{2,ax})$				647(45)		668(8)		N---SF_4, $\nu_{as}(SF_{2,cis})$
										629(19)		SF_4, $\nu_{as}(SF_{2,ax})$
						597(5)				608(8)		Skeletal deformation
						579(19)		572(9)				$\delta_{as}(NC_3)$
										578(12)		SF_5^-, $\nu_{as}(SF_4) + \delta_{as}(NC_3)$
										563sh		
558		535(12)[3]		$\nu_s(SF_{2,ax})$						532(100)		SF_4, $\nu_s(SF_{2,ax})$
								513sh 495(48)		510(68)[z]		N---SF_4, $\nu_s(SF_{2,cis})$ + SF_5^-, $\nu_s(SF_4)$ in phase
532		500(<1)[<1]		$\rho_w(SF_{2,eq})$								
532		494(3)[19]		$\delta_{sc}(SF_{2,eq}) + \delta_{sc}(SF_{2,ax})$								
										452(17)		SF_5^-, $\nu_s(SF_4)$ out of phase
										422(17)		SF_5^-, $\delta_s(SF_4)$ umbrella
						430(11)		436(11) 425(5) 418(3) 399(5)		413sh		$\delta_{as}(NC_3)$
										328(10)		SF_5^-, $\delta_s(SF_4)$ in plane
						337(11)		337(4)		316(10)		$\rho(NC_3)$
475		436(1)[<0.1]		$\tau(SF_2)$								
353		327(<0.1)[10]		$\delta_{sc,\ out\text{-}of\text{-}plane}(SF_{2,ax})$								
228		211(<1)[1]		$\delta_{sc}(SF_{2,eq}) - \delta_{sc}(SF_{2,ax})$				284(60)		280(25)		N---SF_4, $\delta_{sc\ out\text{-}of\text{-}plane}(SF_{2,cis})$
										250(5)		SF_4, $\delta_{sc}(SF_{2,eq}) - \delta_{sc}(SF_{2,ax})$ + SF_5^-, $\delta_{as}(SF_4)$ in plane
								222(2)		220(3)		
								176(6)		149(10)		
								135(2)		120(10)		
								109(9)				

[a] Experimental gas-phase vibrational frequencies and assignments from K. O. Christe, X. Zhang, J. A. Sheehy, R. Bau, *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348 and references therein. The calculated frequencies are essentially the same as in K. O. Christe et al., *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348, but no scaling factors were used for the listed frequencies in the present table. [b] The abbreviations

denote axial (ax), equatorial (eq), symmetric (s), antisymmetric (as), stretch (ν), bend (δ), twist (τ), wagging (ω), rock (ρ), and scissoring (δ_{sc}). For adducted SF_4, F_{apical} denotes the apical fluorine of square pyramidal N---SF_4, F_{trans} and F_{cis} denote the basal fluorine atoms trans and cis to the N donor atom, respectively.

[c] The Raman spectrum was recorded in a m.p. capillary at room temperature.

[d] The Raman spectrum was recorded in a ¼-in. FEP tube at –100 °C. Signals from the FEP sample tube were observed at 291sh, 385(7), 750sh, 1213(2), 1382(5) cm^{-1}. Signals from free, non-adducted SF_4 were observed at 533sh, 868(2), and 889(3) cm^{-1}.

[e] The Raman spectrum was recorded in a ¼-in. FEP tube at –100 °C. Signals from the FEP sample tube were observed at 294(44), 381(35), 386(35), 733(163), 752(5), 1215(15), 1306(29) and 1383(41) cm^{-1}.

[f] Overlap with FEP signal.

Table S4. Observed and Calculated Frequencies for SF_4, $C_6H_{12}N_4$, $C_6H_{12}N_4 \cdot 2SF_4$, and $[C_6H_{12}N_4H]^+[HF_2]^- \cdot SF_4$. Bands Associated with the SF_4 Moiety are Highlighted.

SF_4						$C_6H_{12}N_4$		$C_6H_{12}N_4 \cdot 2SF_4$		$[C_6H_{12}N_4H]^+[HF_2]^- \cdot SF_4$		
exptl[a]		calcd[a,d]		assignments[a,b]		exptl[c]		exptl[d]		exptl[e]		assignments[b]
						2990(2)		3015(11)		3043(7)		
						2954(69)		3004(11)		3031(7)		
						2934(36)		2995(11)		3012sh		
						2921sh		2984(12)		2995(16)		$\nu(CH_2)$ + overtones and
						2909(18)		2960(13)		2962(12)		combination modes
						2894sh				2913(3)		
						2883(15)						
						2873(16)						
						2738(4)						
						2699(2)						
						2678(1)						
						2260(1)						
						2648(2)						Overtones or combination modes
						2632(2)						
						2519(1)						
						2247(1)						
						1988(1)						
								1489(7)				
						1455(30)		1453sh		1455sh		$\delta(CH_2)$
						1441(12)		1446(11)		1447(12)		
						1428(5)						
						1371(8)						$\omega(CH_2)$
						1350(29)		1353(20)		1348(10)		$\tau(CH_2)$
						1326(1)				1322(4)		
						1307(1)		1307(7)				
						1242(10)		1244(11)		1264(3) 1257(3)		ν(C−N)
						1238(14)		1220(8)		1221sh 1214(5)		
										1184(3)		
										1070(4)		
						1043(32)		1049(95)		1030(15)		δ(C−N−C)
						1027sh		1021sh		1021(5)		

						1019(4)		1015(20)		1014(5)		ν(C−N)
						1005(14)		1006sh				
						973(1)		980(5)		979(5) 969(3)		
										874(19)		
892		856(13)[102]		$\nu_s(SF_{2,eq})$				849(89)				bridging SF_4, $\nu_s(SF_{2,eq})$
								843(100) 830sh		843sh 840(94)		terminal SF_4, ν(S−F_1)
						812(5)		818(32)		817(15)		$\rho(CH_2)$
867		825(4)[170]		$\nu_{as}(SF_{2,eq})$				794(76)		795(100)		bridging SF_4,$\nu_{as}(SF_{2,eq})$
								789(70)		785sh		terminal SF_4, ν(S−F_2)
						780(100)		780(83)		775(33)		ν(C−N)
								690(7)				δ(C-N-C)
						672(4)		670(8)		668(8)		
730		703(<1)[630]		$\nu_{as}(SF_{2,ax})$				621(4)		631(3)		$\nu_{as}(SF_{2,ax})$
								579(4)		578(3)		ν_s(FHF)
558		535(12)[3]		$\nu_s(SF_{2,ax})$				522sh 514(48)		519(35)		bridging SF_4, $\nu_s(SF_{2,ax})$
								506(44)[f]				terminal SF_4, $\nu_s(SF_{2,ax})$
532		500(<1)[<1]		$\rho_w(SF_{2,eq})$								$\rho_w(SF_{2,\ eq})$
532		494(3)[19]		$\delta_{sc}(SF_{2,eq})$ + $\delta_{sc}(SF_{2,ax})$								$\delta_{sc}(SF_{2,eq})$ + $\delta_{sc}(SF_{2,ax})$
						513(19)				503(20) 499sh		δ(C-N-C)
						465(36)				459(3)		δ(C-N-C)
475		436(1)[<0.1]		$\tau(SF_2)$				453(8)				terminal SF_4, $\tau(SF_2)$
								448(8)		448(15)		bridging SF_4, $\tau(SF_2)$
353		327(<0.1)[10]		$\delta_{sc,\ out\text{-}of\text{-}plane}(SF_{2,ax})$				363(3)		313(2)		$\delta_{sc\ out\text{-}of\text{-}plane}(SF_{2ax})$
228		211(<1)[1]		$\delta_{sc}(SF_{2,eq})$ − $\delta_{sc}(SF_{2,ax})$				272(6)		276(12)		bridging SF_4, $\delta_{sc}(SF_{2eq})$ − $\delta_{sc}(SF_{2ax})$
								268sh				terminal SF_4, $\delta_{sc}(SF_{2eq})$ − $\delta_{sc}(SF_{2ax})$
								259sh		242(2)		
										166(3)		

[a] Experimental gas-phase vibrational frequencies and assignments from K. O. Christe, X. Zhang, J. A. Sheehy, R. Bau, *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348 and references therein. The calculated frequencies are essentially the same as in K. O. Christe et al., *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348, but no scaling factors were used for the listed frequencies in the present table. [b] The abbreviations denote axial (ax), equatorial (eq), symmetric (s), antisymmetric (as), stretch (ν), bend (δ), twist (τ), wagging (ω), rock (ρ), and scissoring (δ_{sc}). Numbering of fluorine atoms is shown in Figure 2.

[c] The Raman spectrum was recorded in a m.p. capillary at –110 °C.

[d] The Raman spectrum was recorded in a ¼-in. FEP tube at –100 °C. Signals from the FEP sample tube were observed at 294(9), 381(8), 387(9), 733(39), 754sh, 1216(4), 1307(7) cm^{-1}; signals from free SF_4 were observed at 538sh, 860sh and 891(10) cm^{-1}.
[e] The Raman spectrum was recorded in a ¼-in. FEP tube at –100 °C. Signals from the FEP sample tube were observed at 294(9), 381(9), 387(7), 733(34), 752(5), 1303(6) and 1382(12) cm^{-1}; signals from free SF_4 were observed at 535(26), 889(19) and 895sh cm^{-1}.
[f] Overlap with δ(C−N−C) band.