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Structures and Conformations of $CF_3SC(O)F$ and $CF_3SC(O)Cl$: Gas-Phase Electron Diffraction, Vibrational Analysis, and Theoretical Calculations

Karina I. Gobbato,[†,‡] Hans-Georg Mack,[†] Heinz Oberhammer,*,[†] Sonia E. Ulic,[§,||] Carlos O. Della Védova,[§] and Helge Willner[⊥]

Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany, Facultad de Ciencias Exactas, Universidad Nacional de la Plata, Departamento de Quimica, Quimica Inorganica, 1900 La Plata, Argentina, Departamento de Ciencias Básicas, Universidad Nacional de Luján, Argentina, and Institut für Anorganische Chemie, Universität Hannover, Callinstr. 9, D-30167 Hannover, Germany

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The geometric structures and conformational properties of (fluorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)F$, and (chlorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)Cl$, were determined by gas electron diffraction (GED), vibrational spectroscopy (IR(matrix)), and theoretical calculations (HF/3-21G*, HF/6-31G*, MP2/6-31G* ab initio, and BPW91/6-31G*, B3PW91/6-31G* density functional methods). For $CF_3SC(O)F$ a mixture of planar syn and anti conformers occurs with $\Delta G°(\text{GED}) = G°(\text{anti}) - G°(\text{syn}) = 1.3(4)$ kcal mol^{-1} and $\Delta H°(\text{IR}) = H°(\text{anti}) - H°(\text{syn}) = 1.43(12)$ kcal mol^{-1}. Only the planar syn form is obtained in the case of $CF_3SC(O)Cl$. All theoretical approaches reproduce the geometric parameters and conformational properties of both compounds very well. The predicted energy differences $\Delta E = E(\text{anti}) - E(\text{syn})$ vary from 0.98 to 1.24 kcal mol^{-1} for $CF_3SC(O)F$ and from 2.96 to 3.69 kcal mol^{-1} for $CF_3SC(O)Cl$.

Introduction

The geometric structures and conformational properties of compounds, which contain SR groups bonded to sp^2-hybridized carbon atoms, depend primarily on the orbital interaction between the p-shaped sulfur lone pair lp(S) and the π-bond, lp(S) → π^*. This interaction stabilizes synperiplanar and anticlinal (pseudoplanar) conformations of ethenethiol, $HSC(H){=}CH_2$,[1] and of methyl vinyl sulfide, $CH_3SC(H){=}CH_2$.[2,3] The anticlinal conformer is slightly higher in energy for both compounds (Scheme 1).

Similarly, thioformic acid, HSC(O)H, exists as a mixture of planar syn and anti structures.[4] Only planar syn conformers have been observed for *S*-methylthioformate, $CH_3SC(O)H$,[5] for trifluoromethylthioacetic acid, $HSC(O)CF_3$,[6] for trifluorothioacetate chloride, $ClSC(O)CF_3$,[6] and for methyl trifluorothioacetate, $CH_3SC(O)CF_3$.[6] In all these compounds, the sulfur lone pair is parallel or nearly parallel to the C═C or C═O π-bonds and allows a maximum overlap with the π^*-orbitals (Scheme 2).

On the other hand, perfluorination of methyl vinyl sulfide leads to a drastic change of the conformational properties. In $CF_3SC(F){=}CF_2$ the SCF_3 group is oriented perpendicular to the plane of the vinyl group with $\phi(C{=}C{-}S{-}C) = 96.9(12)°$.[7] This change cannot be rationalized by steric interactions only, since F···F contacts between the methyl and vinyl groups are longer than the van der Waals distances for the anticlinal structure. Thus, we assume that the stabilizing lp(S) → π^* interaction is no longer effective in the perfluorinated species, where the sulfur lone pair lies in the plane of the vinyl group, i.e., perpendicular to the π^*-orbital. A perpendicular orientation of the SCF_3 group with respect to the molecular plane has also been observed for bis(trifluoromethylthio)ketene, $(CF_3S)_2C{=}C{=}O$ with $\phi(C{=}C{-}S{-}C) = 95.8(13)°$.[8] In context with the results for these two compounds, which contain SCF_3 groups bonded to sp^2-hybridized carbon, we were interested in the geometries of (fluorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)F$, and of (chlorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)Cl$. We report in this work the gas-phase structures and conformational properties of these two compounds as determined by gas-phase electron diffraction (GED), vibrational spectroscopy, and theoretical methods (ab initio and density functional calculations).

SCHEME 1

synperiplanar anticlinal (pseudoplanar)

SCHEME 2

synperiplanar antiperiplanar

Theoretical Calculations

The planar syn and anti structures of $CF_3SC(O)F$ and $CF_3SC(O)Cl$ were fully optimized with ab initio (HF/3-21G*, HF/6-31G*, MP2/6-31G*) and density functional approaches (BPW91/6-31G*,[9,10] B3PW91/6-31G*[10,11]) using the GAUSSIAN 94 program.[12] Only planar syn and anti conformers

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[†] Universität Tübingen.

[‡] Permanent address: Facultad de Ciencias Exactas, Universidad Nacional de la Plata, Departamento de Quimica, Quimica Inorganica, 1900 La Plata, Argentina.

[§] Universidad Nacional de la Plata.

[||] Universidad Nacional de Luján.

[⊥] Universität Hannover.

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TABLE 1: Experimental and Calculated Geometric Parameters for *syn*-$CF_3SC(O)F$ and Conformational Energy Difference (kcal mol^{-1})

	GED[a]	HF/ 3-21G*	MP2/ 6-31G*	BPW91/ 6-31G*
C=O	1.185(6) p_1	1.177	1.194	1.197
$(C-F)_{mean}$	1.334(3) p_2	1.343	1.344	1.351
ΔCF = (C1−F4) − (C2−F1)	0.014[5][b]	0.005	0.015	0.014
C−F1	1.330(4)	1.342	1.340	1.347
C−F4	1.344(5)	1.347	1.355	1.361
$(S-C)_{mean}$	1.798(4) p_3	1.770	1.793	1.822
ΔSC = (S−C2) − (S−C1)	0.045(11) p_4	0.032	0.050	0.069
S−C1	1.776(7)	1.754	1.768	1.788
S−C2	1.821(7)	1.786	1.818	1.857
S−C=O	132.6(14) p_5	130.0	129.6	130.1
S−C−F4	104.7(10) p_6	106.8	106.8	106.2
O=C−F4	122.7(18)	123.2	123.6	123.7
C−S−C	98.5(6) p_7	97.9	97.1	98.8
F−C−F	108.4(3) p_8	108.6	108.6	109.0
tilt (CF_3)	3.2(7) p_9	4.5	4.4	4.6
% syn	90(5)			
$\Delta G° = G°(\text{anti}) - G°(\text{syn})$	1.3(4)[c]			0.95
$\Delta H° = H°(\text{anti}) - H°(\text{syn})$	1.43(12)[d]			
$\Delta E = E(\text{anti}) - E(\text{syn})$	1.46(12)[d]	0.98	1.24	1.03

[a] r_a distances (Å) and $\angle_\alpha$ angles (degree). Uncertainties are 3σ values and include systematic errors due to constraints. For atom numbering see Figure 2. [b] Theoretical value with estimated uncertainty. [c] From GED. [d] From IR(matrix) spectra; see text.

TABLE 2: Experimental and Calculated Geometric Parameters for *syn*-$CF_3SC(O)Cl$ and Conformational Energy Differences (kcal mol^{-1})

	GED[a]	HF/ 3-21G*	MP2/ 6-31G*	BPW91/ 6-31G*
C=O	1.177(4) p_1	1.184	1.200	1.198
C−F	1.327(3) p_2	1.342	1.339	1.346
C−Cl	1.756(17) p_3	1.760	1.766	1.809
$(S-C)_{mean}$	1.799(8) p_4	1.777	1.794	1.824
ΔSC = (S−C2) − (S−C1)	0.056(23) p_5	0.023	0.048	0.078
S−C1	1.770(12)	1.765	1.770	1.785
S−C2	1.827(12)	1.788	1.818	1.863
S−C=O	129.1(14) p_6	126.9	127.2	128.8
S−C−Cl	108.0(4) p_7	109.6	109.5	108.0
O=C−Cl	122.9(20)	123.5	123.3	123.2
C−S−C	98.9(7) p_8	98.2	97.5	99.3
F−C−F	108.8(3) p_9	108.5	108.6	109.1
tilt (CF_3)	4.8(5) p_{10}	4.5	4.3	4.6
$\Delta E = E(\text{anti}) - E(\text{syn})$		3.67	3.69	2.96

[a] r_a distances (Å) and $\angle_\alpha$ angles (degree). Uncertainties are 3σ values. For atom numbering see Figure 3.

TABLE 3: Interatomic Distances and Vibrational Amplitudes for *syn*-$CF_3SC(O)F$

	distances[a]	amplitude (GED)	amplitude (calcd)[b]
C=O	1.19	0.036[c]	0.036
C−F	1.33−1.34	0.044(2) l_1	0.045
S−C	1.78−1.82	0.053[c]	0.053
F···F	2.16	0.053(5) l_2	0.057
O···F4	2.22	0.053[c]	0.053
S···F	2.48−2.63	0.054(12) l_3	0.070
S···O	2.72	0.046(18) l_4	0.059
C1···C2	2.73	0.087[c]	0.087
O···F2	2.98	0.142(17) l_5	0.245
O···C2	3.00	0.128[c]	0.128
C1···F2	3.03	0.167[c]	0.167
C1···F1	3.91	0.091(16) l_6	0.079
C2···F4	3.91	0.091(16) l_6	0.080
F2···F4	4.27	0.119(16) l_7	0.167
O···F1	4.32	0.122[c]	0.122
F1···F4	4.96	0.084(24) l_8	0.081

[a] Values in Å. Uncertainties are 3σ values. For atom numbering see Figure 2. [b] From BPW91/6-31G* force field. [c] Not refined.

TABLE 4: Interatomic Distances and Vibrational Amplitudes for *syn*-$CF_3SC(O)Cl$

	distances[a]	amplitude (GED)	amplitude (calcd)[b]
C=O	1.18	0.037[c]	0.037
C−F	1.33	0.046(2) l_1	0.046
C−Cl	1.76	0.057[c]	0.057
S−C	1.77−1.83	0.056[c]	0.056
F···F	2.16	0.059(3) l_2	0.057
S···F	2.53−2.64	0.070(9) l_3	0.071
O···Cl	2.59	0.062[c]	0.062
S···O	2.67	0.058[c]	0.058
C1···C2	2.73	0.088[c]	0.088
S···Cl	2.85	0.070(5) l_4	0.076
O···C2	2.93	0.128[c]	0.128
O···F2	2.94	0.32(8) l_5	0.260
C1···F2	3.05	0.14(3) l_6	0.179
C1···F1	3.90	0.11(4) l_7	0.081
O···F1	4.24	0.100[c]	0.100
C2···Cl	4.34	0.092(19) l_8	0.084
Cl···F2	4.70	0.176(16) l_9	0.184
Cl···F1	5.33	0.099(14) l_{10}	0.088

[a] Values in Å. Uncertainties are 3σ values. For atom numbering see Figure 3. [b] From BPW91/6-31G* force field. [c] Not refined.

correspond to minima on the energy hypersurface for which no imaginary frequencies occur. The geometric parameters of the syn conformers, which were obtained at the HF/3-21G*, MP2/6-31G*, and BPW91/6-31G* levels of theory are listed together with the experimental values in Table 1 ($CF_3SC(O)F$) and Table 2 ($CF_3SC(O)Cl$). In the case of the fluorine compound, the potential function for internal rotation around the $S-C(sp^2)$ bond was calculated in the HF/3-21G* approximation. The barrier to internal rotation occurs at $\phi(O{=}C{-}S{-}C) \approx 90°$ and is predicted to be 8.76 kcal mol^{-1} above the syn form. For both molecules the theoretical energy difference between anti and syn structures, $\Delta E = E(\text{anti}) - E(\text{syn})$, depends only slightly on the computational method. For the fluorine compound these energy differences (kcal mol^{-1}) are 0.98 (HF/3-21G*), 1.05 (HF/6-31G*), 1.24 (MP2/6-31G*), 1.03 (BPW91/6-31G*), and 1.06 (B3PW91/6-31G*). The same procedures predict ΔE values of 3.67, 3.68, 3.69, 2.96, and 3.21 kcal mol^{-1} for the chlorine derivative. On the basis of these calculations, we expect to observe a mixture of syn and anti conformers in the case of $CF_3SC(O)F$ and the syn form only for $CF_3SC(O)Cl$. Previous combined GED/vibrational spectroscopy studies of carbonyl compounds such as ClC(O)NCO, FC(O)NCO, or $FC(O)N_3$[13] demonstrated that the C=O vibrational frequencies of the syn and anti forms differ by 35−50 cm^{-1}. The vibrational frequencies of $CF_3SC(O)F$ were calculated with the above-mentioned theoretical methods. The predicted differences in the C=O wavenumbers, $\Delta\nu = \nu(\text{syn}) - \nu(\text{anti})$, are only between 5 and 13 cm^{-1}, i.e., a slightly lower frequency occurs in the anti conformer. The BPW91/6-31G* approximation reproduces the experimental C=O vibrations of the syn conformers for the fluorinated (1855 cm^{-1}) and chlorinated compound (1808 cm^{-1}) most closely. The calculated values are 1854 and 1815 cm^{-1}, respectively. The Cartesian force constants obtained by this method were used to calculate vibrational amplitudes. The Cartesian force constants were transformed to symmetry force constants, and vibrational amplitudes were derived with the program ASYM 40.[14] The theoretical amplitudes are compared to the experimental values in Tables 3 and 4.

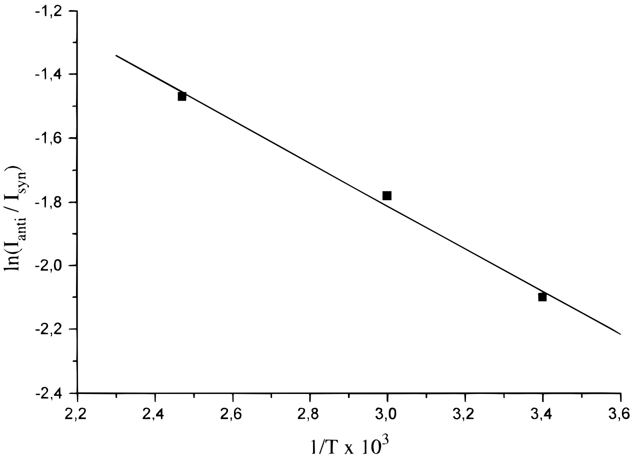

Figure 1. Van't Hoff plot of IR(matrix) data. I_{anti} and I_{syn} correspond to the intensities of the C=O stretching vibrations.

Infrared Spectra

The main interest in the vibrational spectra is the determination of the conformational properties of the title compounds, i.e., the presence of a single conformer or of a mixture of two forms in the gas phase. The vibrational analyses concentrated on the C=O vibrations, which are expected to show the strongest dependence on the conformation of these molecules. In the IR-(gas) spectrum of $CF_3SC(O)F$ the C=O band possesses a weak shoulder to lower wavenumbers, which indicates the presence of a second conformer. Since theoretical calculations predict ν(anti) < ν(syn), we conclude that this shoulder is due to the anti form. For a quantitative analysis of the conformational composition, thermal effusive molecular beams of equilibrium mixtures at different temperatures (20°, 60°, and 120 °C) were trapped in Argon matrices (1:1000). Three bands are observed in the C=O stretching region, the strongest one at 1845 cm^{-1}, a weak band at 1824 cm^{-1}, and the weakest band at 1819 cm^{-1}. The latter band does not change its intensity with temperature or after UV photolysis of the matrix and, thus, is assigned to an impurity. This difference in the C=O frequencies between the two forms observed in the matrix spectra ($\Delta\nu = 21$ cm^{-1}) is larger than that predicted by the theoretical methods ($\Delta\nu =$ 5−13 cm^{-1}). The intensity ratio of the 1824 and 1845 cm^{-1} bands increases with increasing temperature, and $\Delta H° = H°(\text{anti}) - H°(\text{syn}) = 1.43(12)$ kcal mol^{-1} is derived from the van't Hoff plot (Figure 1).

In the case of $CF_3SC(O)Cl$ a narrow B-type band is observed at 1808 cm^{-1} in the IR(gas) spectrum, indicating the presence of a single conformer only. The presence of small amounts of a second form (<5%) cannot be excluded. No matrix spectra were recorded for this compound.

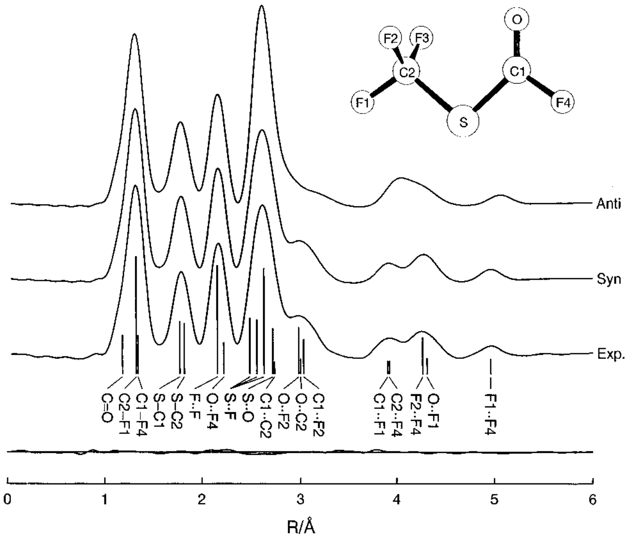

Figure 2. Calculated radial distribution functions for anti and syn forms of $CF_3SC(O)F$ and experimental and difference curves for the mixture (RDF(exp) − RDF(calc)). Molecular model shows the syn conformer. Interatomic distances of the syn structure are indicated by vertical bars.

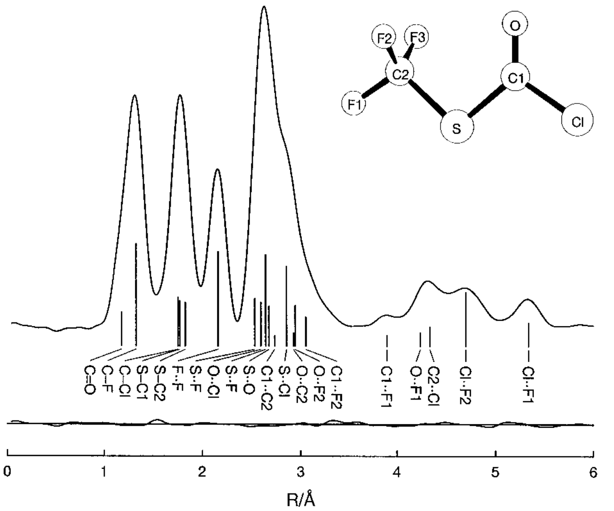

Figure 3. Experimental radial distribution curve and difference curve (RDF(exp) − RDF(calc)) of $CF_3SC(O)Cl$. Molecular model for the syn conformer is shown. Interatomic distances are indicated by vertical bars.

GED Analysis

The radial distribution functions (RDFs) were calculated by Fourier transform of the molecular scattering intensities. Comparison of calculated RDFs for the anti and syn conformers with the experimental curve (Figure 2) demonstrates that the predominant form of $CF_3SC(O)F$ possesses a syn structure. In the case of $CF_3SC(O)Cl$, where only one conformer is expected, the experimental RDF (Figure 3) can be reproduced only with a syn structure. Preliminary geometric parameters derived from the RDFs were refined by least-squares analyses based on the molecular scattering intensities. The intensities were modified with a diagonal weight matrix, and complex scattering factors were used.[15] C_{3v} symmetry was assumed for the CF_3 groups with a possible tilt angle between the C_3 axis and the S−C2 bond direction (for atom numbering see Figures 2 and 3; a positive value implies tilt away from the S−C1 bond). The S−C bond lengths were described by a mean value $(S-C)_{mean} = 0.5[(S-C2) + (S-C1)]$ and by the bond length difference $\Delta SC = (S-C2) - (S-C1)$. In the case of $CF_3SC(O)F$ a mean value for the C−F bond lengths, $(C-F)_{mean} = 0.25[(C1-F) + 3(C2-F)]$ was refined and the difference $\Delta CF = (C1-F) - (C2-F)$ was fixed to the BPW91/6-31G* value. The estimated uncertainty of ±0.005 Å for this difference was taken into account in the experimental uncertainties of the individual C−F bond lengths. Vibrational amplitudes, which either cause high correlations between geometric parameters or are not well determined in the GED experiment, were constrained to the theoretical values. With these constraints 9 or 10 geometric parameters p_i and 8 or 10 vibrational amplitudes l_k were refined simultaneously for $CF_3SC(O)F$ and $CF_3SC(O)Cl$, respectively. The following correlation coefficients had values larger than |0.7|: $CF_3SC(O)F$, $p_4/p_8 = -0.75$, $p_6/l_3 = 0.78$, $p_6/l_4 = 0.76$, and $l_3/l_4 = 0.70$; $CF_3SC(O)Cl$, $p_2/p_3 = 0.72$, $p_3/p_4 = -0.95$, $p_3/p_5 = 0.92$, $p_3/p_6 = 0.85$, $p_4/p_5 = -0.83$, $p_4/p_6 = -0.73$, $p_5/p_6 = 0.83$, and $p_{10}/l_3 = -0.72$. The high correlations in the analysis of $CF_3SC(O)Cl$ cause large standard deviations for p_3

(C−Cl) and p_5 (ΔSC). For $CF_3SC(O)F$ additional least-squares analyses were performed for mixtures of syn and anti conformers. The differences between bond lengths and bond angles of the two forms were fixed to the BPW91/6-31G* values. Considerable differences occur for S−C=O (−7.0°), S−C−F4 (+7.1°), and C−S−C (+4.6°). The agreement factors decrease slightly for 10% contribution of the anti form and increase for larger contributions. The uncertainty is estimated to be ±5%. This conformational composition corresponds to $\Delta G° = G°(\text{anti}) - G°(\text{syn}) = 1.3(4)$ kcal mol^{-1}. The final results of the GED analyses are listed in Tables 1 and 2 (geometric parameters p_i) and Tables 3 and 4 (vibrational amplitudes l_k).

Discussion

The predominant conformer of both carbonyltrifluoromethylsulfanes, $CF_3SC(O)F$ and $CF_3SC(O)Cl$, possesses a planar syn structure. According to the GED analysis, a small amount of 10(5)% of the planar anti conformer is present in the fluorine derivative ($\Delta G° = G°(\text{anti}) - G°(\text{syn}) = 1.3(4)$ kcal mol^{-1}). A more accurate value was derived for the enthalpy difference between the two forms from the analysis of IR(matrix) spectra ($\Delta H° = 1.43(12)$ kcal mol^{-1}). From this we obtain $\Delta G°$(IR) = 1.38(12) kcal mol^{-1} if the theoretical (BPW91/6-31G*) entropy difference, $\Delta S° = 0.18$ cal mol^{-1} K^{-1}, is used. This result is in perfect agreement with the corresponding GED value. For comparison with the calculated ΔE values, the theoretical (BPW91/6-31G*) zero-point vibrations and thermodynamical data were used to convert $\Delta H°$(IR) to ΔE(IR) ($\Delta E - \Delta H° = 0.03$ kcal mol^{-1}). The experimental energy difference, ΔE(IR) = 1.46(12) kcal mol^{-1}, is slightly larger than all theoretical predictions ($\Delta E = 0.98-1.24$ kcal mol^{-1}) for $CF_3SC(O)F$. In the case of $CF_3SC(O)Cl$, the theoretical energy differences ΔE vary from 2.96 to 3.69 kcal mol^{-1}. This is qualitatively in agreement with the GED and IR analyses, where no second conformer was observed.

The present conformational studies for CF_3S-substituted carbonyls lead to the same result as those of previous investigations for compounds of the type RSC(O)X. In all experimental studies only planar structures were observed with the syn forms (S−R syn with respect to C=O) being favored.[6] Thus, fluorination does not lead to a change in the conformational properties of carbonyl compounds, RSC(O)X, as was observed in the case of methyl vinyl sulfide.

Experimental Section

(Fluorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)F$, was prepared by the reaction of FC(O)SCl with CF3COOAg (Solvay) and decarboxylation of the resulting CF3C(O)OSC(O)F by irradiation with UV light.[16,17] The product was purified by fractional condensation, and the purity was checked by IR and ^{19}F NMR spectroscopy. Gas-phase and matrix IR spectra were recorded with an FTIR spectrometer, IFS 66v (Bruker).[18]

(Chlorocarbonyl)trifluoromethylsulfane, $CF_3SC(O)Cl$, was obtaind by reaction of $CF_3SC(O)F$ with BCl_3 for 2 days at room temperature.[16,17] The purification of the compound was performed by trap-to-trap distillation, and the purity was checked by IR and ^{19}F NMR spectroscopy.

The electron diffraction intensities were recorded with a gas diffractograph KD-G2[19] at two nozzle-to-plate distances (50 and 25 cm) with an accelerating voltage of ca. 60 kV. The sample reservoirs were kept at −60 °C ($CF_3SC(O)F$) and −40 °C ($CF_3S-C(O)Cl$). The inlet system and the gas nozzle were maintained at room temperature. The photographic plates (Kodak Electron Image Plates, 13 cm × 18 cm) were analyzed by the usual procedures.[20] Averaged molecular intensities in the s-ranges 2−18 and 8−35 Å^{-1} in intervals of $\Delta s = 0.2$ Å^{-1} are shown in Figures 4 and 5 ($s = (4\pi/\lambda)\sin(\vartheta/2)$, λ = electron wavelength, ϑ = scattering angle).

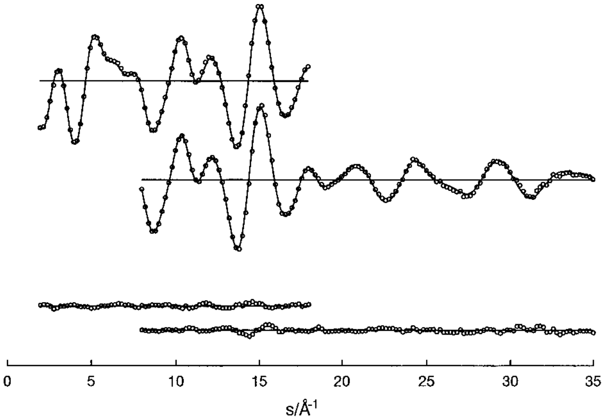

Figure 4. Experimental (dots) and calculated (full line) molecular scattering intensities of $CF_3SC(O)F$ for long (above) and short (below) nozzle-to-plate distances and differences.

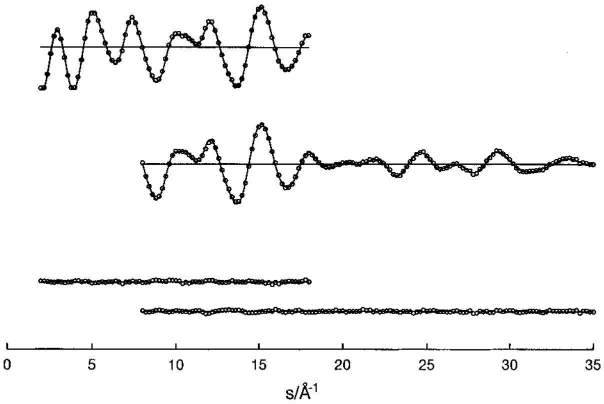

Figure 5. Experimental (dots) and calculated (full line) molecular scattering intensities for long (above) and short (below) nozzle-to-plate distances and differences.

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References and Notes

(1) Almond, V.; Permanand, R. R.; MacDonald, J. N. *J. Mol. Struct.* **1985**, *128*, 337.
(2) Derissen, J. L.; Bijen, J. M. *J. Mol. Struct.* **1973**, *16*, 289.
(3) Samdal, S.; Seip, H. M.; Torgrimsen, T. *J. Mol. Struct.* **1979**, *57*, 105.
(4) Hocking, W. H.; Winnewisser, G. *Z. Naturforsch.* **1977**, *32A*, 1108.
(5) Jones, G. I. L.; Lister, D. G.; Owen, N. L.; Gerry, M. C. L.; Palmieri, P. *J. Mol. Spectrosc.* **1976**, *60*, 348.
(6) Gobbato, K. I.; Della Védova, C. O.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1996**, *35*, 6152.
(7) Olleta, A.; Haas, A.; Oberhammer, H. *Chem. Ber.* **1995**, *128*, 803.
(8) Korn, M.; Mack, H.-G.; Praas, H. W.; Della Védova, C. O.; Oberhammer, H. *J. Mol. Struct.* **1995**, *352/353*, 145.
(9) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(10) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, H.; Al-Laham, A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) Mack, H.-G.; Oberhammer, H.; Della Védova, C. O. *J. Mol. Struct.* **1989**, *200*, 277. Mack, H.-G.; Della Védova, C. O.; Willner, H. *J. Mol. Struct.* **1993**, *291*, 197.

(14) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(15) Haase, J. *Z. Naturforsch.* **1970**, *25A*, 936.

(16) Haas, A.; Helmbrecht, J.; Klug, W.; Koch, B; Reinke, H.; Sommerhoff, *J. Fluorine Chem.* **1973/74**, *3*, 383.

(17) Sommerhoff, J. Ph.D. Thesis, Ruhr-Univeristät Bochum, Germany, 1972.

(18) Bodenbinder, M.; Ulic, S. E.; Willner, H. *J. Phys. Chem.* **1994**, *98*, 6441.

(19) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London 1976; Vol. 4, p 24.

(20) Oberhammer, H; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.