

## Anomeric Effects in Bis(fluorooxy)difluoromethane

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Received September 4, 1996<sup>⊗</sup>

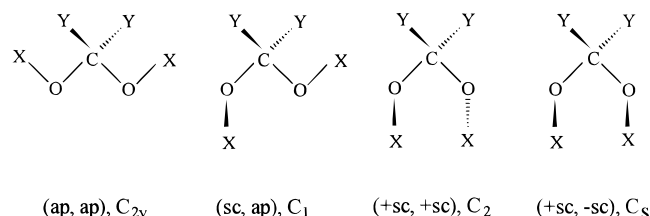
**Abstract:** The geometric structure and conformational properties of bis(fluorooxy)difluoromethane, CF<sub>2</sub>(OF)<sub>2</sub>, were determined by gas electron diffraction and theoretical methods (ab initio and density functional calculations). The electron diffraction intensities are reproduced best by a mixture of 70(10)% (+sc,+sc) and 30(10)% (sc,ap) conformers, corresponding to  $\Delta H^\circ = H^\circ(\text{sc,ap}) - H^\circ(+\text{sc},+\text{sc}) = 0.9(3) \text{ kcal mol}^{-1}$ . This experimental result is reproduced very well by HF/6-31G\* and MP2/6-31G\* calculations ( $\Delta E = 0.7 \text{ kcal mol}^{-1}$ ), but not by the HF/3-21G and the density functional (SVWN/6-311G\*, BLYP/6-311G\*, B3LYP/6-311+G\*) approximations. In addition, the conformational properties of CF<sub>2</sub>(OH)<sub>2</sub> and CH<sub>2</sub>(OF)<sub>2</sub> were investigated theoretically. The experimental and theoretical results are discussed in terms of anomeric effects.

## Introduction

Simple structural concepts such as covalent radii, hybridization, or the VSEPR model provide for many molecules a good estimate for bond lengths and bond angles. On the other hand, no such simple concepts exist for the prediction of the dihedral angle of an A–B–C–D chain. This angle depends on various interactions between substituents, bonds, and lone pairs. If one of the central atoms, i.e. B, possesses one or more lone pairs, the generalized anomeric effect may have a large influence on this dihedral angle.<sup>1</sup> The origin of this stereoelectronic effect is negative hyperconjugation, i.e., orbital interaction between a lone pair at B and the antibonding  $\sigma^*$  orbital of the C–D bond. This interaction leads to a strong preference of the trans orientation of the C–D bond relative to the lone pair. The influence of the anomeric effect on the conformational properties has been studied extensively by theoretical methods for the model compound dihydroxymethane (methanediol), CH<sub>2</sub>(OH)<sub>2</sub>.<sup>2–7</sup> Depending on the orientation of the O–X bonds, the following four conformations have to be considered for CY<sub>2</sub>(OX)<sub>2</sub> compounds:

If we describe the oxygen lone pairs by two energetically equal sp<sup>3</sup> orbitals (“rabbit ears”),<sup>8</sup> two lp(O) →  $\sigma^*(\text{C–Y})$

Chart 1



interactions occur for the antiperiplanar orientation of an O–X bond. For the synclinal orientation of an O–X bond one lp(O) →  $\sigma^*(\text{C–Y})$  and one lp(O) →  $\sigma^*(\text{C–O})$  interaction occur. Thus, the preferred structure primarily depends on the competition between these two different orbital interactions. Other effects such as bond–antibond interactions and dipole interactions are considered to have a minor influence. Ab initio calculations for dihydroxymethane (X = Y = H) predict a strong preference of the (+sc,+sc) conformer by 3.2 to 5.0 kcal mol<sup>-1</sup> relative to the (sc,ap) form, depending on the computational method. This demonstrates that the lp(O) →  $\sigma^*(\text{C–O})$  interaction is much stronger than the lp(O) →  $\sigma^*(\text{C–H})$  interaction. The (+sc, -sc) conformer possesses an energy which is similar to that of the (sc,ap) structure, whereas the (ap,ap) form is predicted to be much higher in energy (7–12 kcal mol<sup>-1</sup>) and does not correspond to a minimum on the energy hypersurface. Experimental studies of dimethoxymethane (X = Me, Y = H)<sup>9</sup> and 2,2-dimethoxypropane (X = Y = Me)<sup>10</sup> observe only (+sc,+sc) structures for these compounds, demonstrating again the dominance of the lp(O) →  $\sigma^*(\text{C–O})$  interaction over lp(O) →  $\sigma^*(\text{C–H})$  or lp(O) →  $\sigma^*(\text{C–C})$  interactions.

Theoretical and experimental investigations of fluorinated ethers CH<sub>2</sub>FOCH<sub>3</sub><sup>11–13</sup> and CF<sub>3</sub>OCH<sub>3</sub><sup>14</sup> have shown that their structures and conformations are affected by lp(O) →  $\sigma^*(\text{C–$

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, January 1, 1997.

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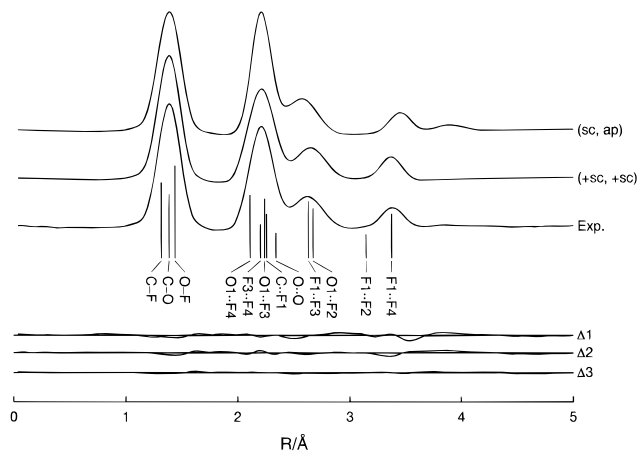
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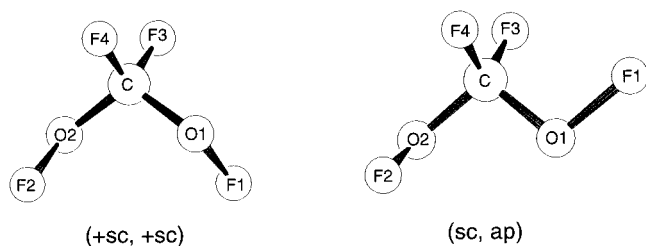
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**Figure 1.** Calculated radial distribution functions for (sc,ap) and (+sc,+sc) conformers and the experimental curve.  $\Delta 1$  = difference curve for the (sc,ap) conformer,  $\Delta 2$  = difference curve for the (+sc,+sc) conformer,  $\Delta 3$  = difference curve for the mixture. Interatomic distances for the predominant (+sc,+sc) structure are indicated by vertical bars.



**Figure 2.** Molecular models and atom numbering for (+sc,+sc) and (sc,ap) conformers of  $\text{CF}_2(\text{OH})_2$ .

F) interactions, which are estimated to possess a similar strength as  $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{C}-\text{O})$  interactions. In the present study we report the conformational properties of fluorinated derivatives of dihydroxymethane. In these compounds competition between  $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{C}-\text{O})$  and  $\text{lp}(\text{O}) \rightarrow \sigma^*(\text{C}-\text{F})$  interactions is expected. We present a gas-phase electron diffraction analysis of bis(fluorooxy)difluoromethane,  $\text{CF}_2(\text{OF})_2$ , and various theoretical calculations for  $\text{CF}_2(\text{OF})_2$ ,  $\text{CH}_2(\text{OF})_2$ , and  $\text{CF}_2(\text{OH})_2$ .

### Electron Diffraction Analysis for $\text{CF}_2(\text{OF})_2$

The radial distribution function (RDF) was calculated by Fourier transform of the molecular scattering intensities with an artificial damping function  $\exp(-\gamma s^2)$ ,  $\gamma = 0.0019 \text{ \AA}^2$ . Comparison of the experimental curve with functions which were calculated for the four possible conformations demonstrates that the (+sc,+sc) structure is the prevailing form. The calculated RDFs (Figure 1) for the (+sc,+sc) and (sc,ap) conformers are rather similar. Small differences occur in the intensities and positions of the peaks around 2.6 and 3.4  $\text{\AA}$ . Furthermore, the (sc,ap) curve possesses a peak around 3.9  $\text{\AA}$ , which corresponds to the  $\text{F1}\cdots\text{F2}$  distance (for atom numbering see Figure 2). A weak feature at this distance in the experimental curve indicates the presence of an appreciable amount of this conformer. In the least squares analyses the molecular intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used.<sup>15</sup> The geometry of the main conformation (+sc,+sc) was constrained to  $C_2$  symmetry and was described by the three bond lengths, the  $\text{O}-\text{C}-\text{O}$  and  $\text{C}-\text{O}-\text{F}$  bond angles, a mean  $\text{O}-\text{C}-\text{F}$  angle, and the dihedral angle  $\text{O}-\text{C}-\text{O}-\text{F}$ . Ab initio calculations (see below) predict a rather large twist of the  $\text{CF}_2$  group and the

resulting difference between the two types of  $\text{O}-\text{C}-\text{F}$  angles,  $\Delta\text{OCF} = (\text{O1}-\text{C}-\text{F3}) - (\text{O1}-\text{C}-\text{F4})$ , was set to the MP2/6-31G\* value in the experimental analysis. The uncertainty of this theoretical value is estimated to be  $\pm 2^\circ$ . Differences between the structural parameters for the (+sc,+sc) and (sc,ap) conformers were constrained to the MP2/6-31G\* results. These differences are remarkably large for the  $\text{O}-\text{C}-\text{O}$  angle ( $-9.2^\circ$ ) and for one of the  $\text{O}-\text{C}-\text{F}$  angles ( $+9.0^\circ$ ). The dihedral angles for the minor conformer were set to the theoretical values ( $\text{O1}-\text{C}-\text{O2}-\text{F2} = 67.8^\circ$ ,  $\text{O2}-\text{C}-\text{O1}-\text{F1} = 181.6^\circ$ ). Vibrational amplitudes were collected in groups according to their distances and according to the amplitudes derived from the ab initio force field (see below). Because of large correlations the amplitudes for the bonded distances were fixed to the theoretical values in the least-squares analyses, but varied within a range of  $\pm 0.005 \text{ \AA}$  in order to estimate the systematic errors for the bond lengths due to these constraints. The amplitudes for the  $\text{C}\cdots\text{F1}$  and  $\text{F1}\cdots\text{F2}$  distances were not refined. With these assumptions seven geometric parameters  $p_i$  and three vibrational amplitudes  $l_k$  were refined simultaneously, and the following correlation coefficients possessed values larger than  $|0.6|$ :  $p_1/p_2 = -0.62$ ,  $p_1/p_3 = 0.66$ ,  $p_2/p_3 = -0.66$ ,  $p_4/l_1 = -0.61$ , and  $p_6/l_1 = -0.74$ . Least-squares refinements were performed for different ratios of the (+sc,+sc) and (sc,ap) conformers. The agreement factor for the long-camera-distance data was a minimum for a 70%:30% composition. The uncertainty was estimated to be  $\pm 10\%$ . This corresponds to a free enthalpy difference of  $\Delta G^\circ = G^\circ(\text{sc,ap}) - G^\circ(+\text{sc,+sc}) = 0.5(3) \text{ kcal mol}^{-1}$ . If entropy differences between the two conformations are neglected, except for the different multiplicities (2 for (+sc,+sc) and 4 for (sc,ap)), an enthalpy difference of  $\Delta H^\circ = 0.9(3) \text{ kcal mol}^{-1}$  is derived. The final results are listed in Tables 1 (geometric parameters) and 2 (vibrational amplitudes).

### Theoretical Calculations

The conformational properties of  $\text{CF}_2(\text{OF})_2$ ,  $\text{CH}_2(\text{OF})_2$ , and  $\text{CF}_2(\text{OH})_2$  were investigated theoretically applying standard ab initio methods (HF/3-21G, HF/6-31G\*, and MP2/6-31G\*) and density functional calculations (DFT, local, and non-local approximations). For  $\text{CF}_2(\text{OF})_2$  additional calculations were performed with Becke's 3-parameter hybrid method. All structures were fully optimized for the four conformations shown in Chart 1 and the energies relative to the (+sc,+sc) structures are collected in Table 3. The program system GAUSSIAN92/DFT<sup>21</sup> was used for all calculations. The geometric parameters of the (+sc,+sc) conformer of  $\text{CF}_2(\text{OF})_2$  as obtained by the HF/3-21G, HF/6-31G\*, MP2/6-31G\*, and B3LYP/6-311+G\* methods are compared to the experimental values in Table 1. Cartesian force constants for the main conformer were calculated with the HF/3-21G method and transformed into symmetry force constants. These values were scaled with the usual factor except for the two torsional constants. Vibrational amplitudes were derived with the program ASYM40.<sup>22</sup>

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**Table 1.** Experimental and Calculated Geometric Parameters for the (+sc,+sc) Conformer of CF<sub>2</sub>(OF)<sub>2</sub> (for Atom Numbering See Figure 2)

	GED <sup>a</sup>		HF/3-21G	HF/6-31G*	MP2/6-31G*	B3LYP/6-311+G*
C–F	1.317(5)	<i>p</i> <sub>1</sub>	1.328	1.303	1.332	1.330
C–O	1.387(6)	<i>p</i> <sub>2</sub>	1.396	1.367	1.391	1.393
O–F	1.440(5)	<i>p</i> <sub>3</sub>	1.431	1.365	1.441	1.428
O–C–O	115.0(9)	<i>p</i> <sub>4</sub>	113.4	114.1	115.1	115.4
C–O–F	105.7(4)	<i>p</i> <sub>5</sub>	104.4	105.9	103.3	106.0
(O–C–F) <sub>mean</sub>	107.1(4)	<i>p</i> <sub>6</sub>	108.3	108.1	107.7	107.7
Δ(OCF) = (O1–C–F3) – (O1–C–F4)	10.0[20] <sup>b</sup>		7.5	7.8	10.0	10.2
O1–C–F3	112.1(11)		112.0	112.0	112.7	112.8
O1–C–F4	102.1(11)		104.5	104.2	102.7	102.6
F–C–F	113.0(9)		110.7	110.7	111.1	110.8
O–C–O–F	55.3(21)	<i>p</i> <sub>7</sub>	58.6	59.0	57.9	56.9
% (sc,ap)	30(10)					
Δ <i>H</i> <sup>o</sup> /Δ <i>E</i> (kcal mol <sup>-1</sup> ) <sup>c</sup>	0.9(3)		–0.01	0.72	0.71	0.36

<sup>a</sup> *r*<sub>a</sub> distances (Å) and ∠<sub>α</sub> angles (deg), uncertainties are 3σ values and include systematic errors due to constraints. <sup>b</sup> Theoretical value with estimated uncertainty. <sup>c</sup> Δ*H*<sup>o</sup> = *H*<sup>o</sup>(+sc,+sc) – *H*<sup>o</sup>(sc,ap).

**Table 2.** Interatomic Distances and Vibrational Amplitudes for the (+sc,+sc) Conformer of CF<sub>2</sub>(OF)<sub>2</sub> (for Atom Numbering See Figure 2)

distance	amplitudes		
	GED		HF/3-21G
C–F	1.32	0.043[5] <sup>a</sup>	0.043
O–F	1.44		0.043
C–O	1.39	0.048[5] <sup>a</sup>	0.048
O1••F4	2.11	0.055(6)	0.060
F3••F4	2.21		0.058
O1••F3	2.24		0.062
O••O	2.34		0.062
C••F1	2.25	0.067 <sup>b</sup>	0.067
F1••F3	2.63	0.122(6)	0.137
O1••F2	2.67		0.129
F1••F2	3.13	0.228 <sup>b</sup>	0.228
F1••F4	3.37	0.071(6)	0.061

<sup>a</sup> Theoretical value with estimated uncertainty in square brackets. <sup>b</sup> Not refined.

## Discussion

The most stable structure of CF<sub>2</sub>(OF)<sub>2</sub> is the (+sc,+sc) conformer, as in the case of the parent compound CH<sub>2</sub>(OH)<sub>2</sub>. The energy difference between the (sc,ap) and the (+sc,+sc) form is much smaller in the fluorinated derivative (Δ*H*<sup>o</sup> = 0.9(3) kcal mol<sup>-1</sup> vs Δ*E* = 3.2–5.0 kcal mol<sup>-1</sup> in CH<sub>2</sub>(OH)<sub>2</sub>). The experimental enthalpy difference is reproduced very well by HF/6-31G\* and MP2/6-31G\* calculations, whereas the HF/3-21G approximation and one DFT method predict a predominance of the (sc,ap) form (see Table 3). The small experimental energy difference between these two structures indicates that the stabilizing energies of the two relevant anomeric effects lp(O) → σ\*(C–O) and lp(O) → σ\*(C–F) are very similar in this compound. All our calculations predict the two other conformers (ap,ap) and (+sc,+sc) to be appreciably higher in energy, in agreement with the experiment, where no contributions of these structures are observed. Only the HF/3-21G approach results in a low relative energy (0.22 kcal mol<sup>-1</sup>) for the (ap,ap) form.

The short C–F bonds can be explained by the strong electron-withdrawing effect of the two OF groups. C–F bonds in CF<sub>2</sub>X<sub>2</sub> compounds depend strongly on the electronegativity of the substituents X: 1.3601(14) Å in CF<sub>2</sub>H<sub>2</sub>,<sup>23</sup> 1.3188(4) Å in CF<sub>4</sub>,<sup>24</sup> and 1.317(5) Å in CF<sub>2</sub>(OF)<sub>2</sub>. The O–F bond lengths in CF<sub>2</sub>(OF)<sub>2</sub> (1.440(5) Å) are longer than the corresponding bonds in other hypofluorites: 1.418(5) Å in FC(O)OF,<sup>25</sup> 1.409(5) Å in

FONO<sub>2</sub>,<sup>26</sup> and 1.421(6) Å in CF<sub>3</sub>OF.<sup>27</sup> The quality of the predictions of the four theoretical methods, whose results are collected in Table 1, is different with respect to structural and conformational properties. The MP2 approximation predicts the structure, with the exception of the C–F bond distance, reasonably well and results in perfect agreement with the experimental conformational composition. The same agreement with respect to the experimental energy difference is obtained by the HF/6-31G\* approach, but the theoretical bond lengths deviate by up to 0.08 Å (O–F = 1.440(6) Å vs 1.365 Å). On the other hand, the HF/3-21G and B3LYP/6-311+G\* methods reproduce the experimental geometry as well as the MP2 calculations, but do not lead to a correct conformational composition.

According to the theoretical calculations for CH<sub>2</sub>(OF)<sub>2</sub> (Table 3) again the (+sc,+sc) form is the most stable conformation, but in this compound the (+sc,–sc) form represents the next stable structure (Δ*E* ≈ 1 kcal mol<sup>-1</sup>). The relative energy of the (ap,ap) conformer (Δ*E* ≈ 9 to 17 kcal mol<sup>-1</sup>) is similar to that in the parent compound (Δ*E* ≈ 7–12 kcal mol<sup>-1</sup>). The ab initio calculations predict the relative energy of the (sc,ap) form to be intermediate (Δ*E* ≈ 4–5 kcal mol<sup>-1</sup>). This conformation does not correspond to stable structures according to the DFT methods. These theoretical relative energies for CH<sub>2</sub>(OF)<sub>2</sub> demonstrate again that the lp(O) → σ\*(C–O) interaction is much stronger than the lp(O) → σ\*(C–H) interaction, as observed for the parent compound CH<sub>2</sub>(OH)<sub>2</sub>.

The conformational properties of CF<sub>2</sub>(OH)<sub>2</sub> differ drastically from those of the other CX<sub>2</sub>(OY)<sub>2</sub> derivatives. Depending on the computational approach, the (sc,ap) or (ap,ap) conformations represent the most stable structures (Table 3). The HF/3-21G method predicts a synperiplanar–antiperiplanar (sp,ap) form with O–C–O–H dihedral angles of 0° and 180° to be lowest in energy. The least stable conformation is the (+sc,–sc) conformer. The relative stabilities of the four conformations of this compound indicate that in this case the lp(O) → σ\*(C–F) interaction dominates strongly over the lp(O) → σ\*(C–O) interaction.

## Experimental Section

F<sub>2</sub>C(OF)<sub>2</sub> was synthesized by fluorination of CO<sub>2</sub> in the presence of CsF.<sup>28</sup> The compound was purified by trap-to-trap distillation, and the purity was checked by IR(gas) and <sup>19</sup>F-NMR spectroscopy.

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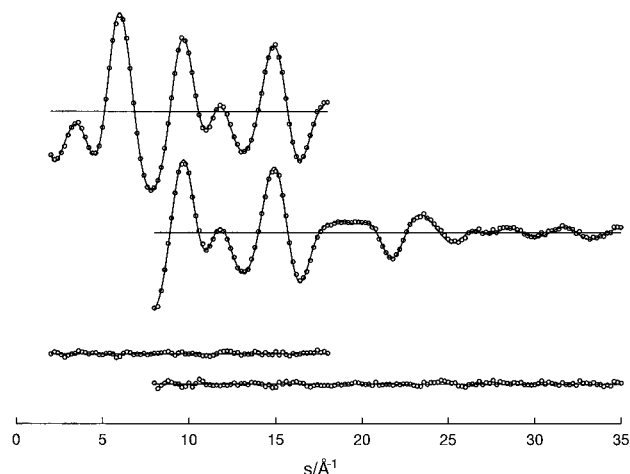
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**Table 3.**  $\text{CY}_2(\text{OX})_2$  Compounds: Calculated Conformational Energies ( $\text{kcal mol}^{-1}$ ) Relative to the (+sc,+sc) Structure<sup>a</sup>

$\text{CY}_2(\text{OX})_2$	HF/3-21G	HF/6-31G*	MP2/6-31G*	SVWN/6-311G* <sup>b</sup>	BLYP/6-311G* <sup>c</sup>	B3LYP/6-311+G* <sup>d</sup>
$\text{CF}_2(\text{OF})_2$ (+sc,+sc)	0.00	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	0.00	<b>0.00</b>
(sc,ap)	<b>-0.01</b>	0.72	0.71	0.15	<b>-0.27</b>	0.36
(ap,ap)	0.22	1.86	2.55	4.70	4.29	3.37
(+sc,-sc)	2.08	2.79	2.84	3.47	3.14	3.17
$\text{CH}_2(\text{OF})_2$ (+sc,+sc)	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
(sc,ap)	4.08	4.11	4.89	e	e	
(ap,ap)	9.06	9.76	12.13	17.47	14.79	
(+sc,-sc)	0.72	1.14	0.80	1.18	1.13	
$\text{CF}_2(\text{OH})_2$ (+sc,+sc)	0.00	0.00	0.00	0.00	0.00	
(sc,ap)	<b>-2.39<sup>f</sup></b>	<b>-1.00</b>	-1.09	<b>-1.56</b>	-1.44	
(ap,ap)	-1.16	-0.78	<b>-1.17</b>	-1.35	<b>-1.66</b>	
(+sc,-sc)	e	3.62	3.69	3.76	3.36	

<sup>a</sup> Bold numbers refer to the global minimum. <sup>b</sup> Local DFT approximation (LDFT); Slater's exchange functional<sup>16</sup> combined with the correlation functional of Vosko, Wilk, and Nusair.<sup>17</sup> <sup>c</sup> Non-local DFT approximation; LDFT combined with the gradient-corrected functionals of Becke (exchange)<sup>18</sup> and of Lee, Yang, and Parr (correlation).<sup>19</sup> <sup>d</sup> Hybrid method reported by Becke,<sup>20</sup> combined with the gradient-corrected correlation functional of Lee, Yang, and Parr. <sup>e</sup> Does not correspond to a stable structure. <sup>f</sup> The (sc,ap) conformer converges to a (sp,ap) structure with O-C-O-H dihedral angles of 0° and 180°.

**Figure 3.** Experimental (dots) and calculated (full line) molecular intensities and difference for  $\text{CF}_2(\text{OF})_2$ .

The electron diffraction intensities were recorded with a Gasdiffractograph KD-G2<sup>29</sup> at two nozzle-to-plate distances (50 and 25 cm)

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

with an accelerating voltage of ca. 60 kV. The sample reservoir was kept at  $-115^\circ\text{C}$  and the inlet system and the gas nozzle were maintained at room temperature. The photographic plates (Kodak Electron Image Plates,  $13 \times 18$  cm) were analyzed by the usual procedures.<sup>30</sup> Averaged molecular intensities in the  $s$ -ranges 2–18 and 8–35  $\text{\AA}^{-1}$  in intervals of  $\Delta s = 0.2 \text{\AA}^{-1}$  are shown in Figure 3 ( $s = 4\pi/\lambda \sin(\vartheta/2)$ ,  $\lambda$  is the electron wavelength,  $\vartheta$  is the scattering angle).

**Acknowledgment.** H.G.M. and H.O. gratefully acknowledge generous financial support by the Deutsche Forschungsgemeinschaft (DFG). C.O.D.V. thanks the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, República Argentina) and the Facultad de Ciencias Exactas (Universidad Nacional de La Plata). H.G.M., H.O., and C.O.D.V. thank the Fundación Antorchas (República Argentina) for financial support. H.G.M. and H.O. thank the Research Centre Jülich (KFA, Germany) for access to substantial computer time. K.I.G. thanks the DAAD (Germany) for the grant of a "Sandwich" fellowship. We thank Prof. H. Willner (University of Hannover, Germany) for his support in the synthesis of  $\text{CF}_2(\text{OF})_2$ .

JA963106W

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