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The Equilibrium between *cis*- and *trans*-Fluoroformyl Hypofluorite, FC(O)OF. Thermodynamic Properties, Molecular Structures, and Vibrational Spectra

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From equilibrium mixtures of *cis*- and *trans*-FC(O)OF, complete sets of the nine fundamentals and several combinations were measured by gas phase IR, matrix IR and low-temperature Raman spectroscopy. Assignment of bands to the *cis* or *trans* conformer was achieved by gas band contour analysis and by comparison between observed and ab initio calculated (MP2/6-31G*) vibrational spectra. The enthalpy difference between *cis*- and *trans*-FC(O)OF amounts to $\Delta H^\circ = H^\circ(cis) - H^\circ(trans) = 4.9(3)$ kJ mol^{-1} derived from the matrix infrared bands of thermal effusive molecular beams at different temperatures quenched as argon matrices. The respective entropy difference amounts to 1.45 J mol^{-1} K^{-1} as calculated from statistical thermodynamics. A normal-coordinate analysis was performed for both conformers using their fundamental wavenumbers of different isotopomers. The molecular structures of both conformers at 298 K (14% *cis*-, 86% *trans*-FC(O)OF) were determined by gas electron diffraction and theoretical calculations. Ab initio calculations at the HF and MP2 levels overestimate the energy difference between the two conformers, whereas local and nonlocal density functional theory calculations predict a reversed conformational stability. The bonding properties of *cis*- and *trans*-FC(O)OF are discussed in terms of their force constants and bond lengths.

Introduction

Fluoroformyl hypofluorite, FC(O)OF, was first synthezised by Cauble and Cady,[1] who characterized the compound by chemical analysis, its physical properties, and infrared and NMR spectroscopy. It was viewed as an unstable molecule, which hindered further investigations. However, recently, the compound became of interest as a precursor in the synthesis of difluorodioxirane, CF_2O_2,[2] which may be involved in the stratospheric chemistry of fluorocarbon hydrides.[3]

An improved synthesis and purification of FC(O)OF enabled us to reinvestigate its properties, detect its two conformers by ^{19}F NMR spectroscopy, and study the mechanism of its formation using ^{18}O-isotopically enriched precursors.[4]

In this study, we report the determination of the geometric structures of both conformers by gas electron diffraction (GED) and harmonic force fields derived from matrix IR spectra of various isotopic species. Furthermore, we investigated the equilibrium between *cis*- and *trans*-FC(O)OF using FTIR spectroscopy by quenching thermal effusive molecular beams in argon matrices at 10 K, similar to techniques described previously.[5] The experimental investigations are supplemented by theoretical calculations.

Experimental Section

The synthesis and purification of FC(O)OF are as described previously.[4] The sample used contained the impurities: 5% FC(O)OOF, 1% CO_2 as detected by ^{19}F NMR and IR spectroscopy.

Caution! Although no explosion occurred in the course of this study, fluoroformyl hypofluorite is potentially explosive like other hypofluorites,[6] especially in the presence of oxidizable materials. It should be handled with proper safety precaution and only in millimolar quantities.

The electron diffraction intensities were recorded with a Gasdiffractograph KD-G2 at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV.[7] The electron wavelength was calibrated by ZnO powder diffraction. The sample reservoir was cooled to −110 °C, and the stainless steel inlet system and nozzle were kept at room temperature. The camera pressure during the experiments was ca. 1.5×10^{-5} mbar. The photographic plates were analyzed by standard procedures.[8] Numerical values for total scattering intensities are available as supplementary material, and averaged molecular intensities in the *s* ranges 2−18 and 8−35 Å^{-1} in intervals of $\Delta s = 0.2$ Å^{-1} are presented in Figure 1.

Details of the matrix-isolation apparatus are given elsewhere.[5] Gas phase and matrix infrared spectra were recorded with a resolution of 1.3 cm^{-1} using an FTIR spectrometer, IFS 66v (Bruker). A DTGS detector together with a Ge/KBr beam splitter operated in the region 4000−400 cm^{-1} and 64 scans were coadded for each spectrum. A

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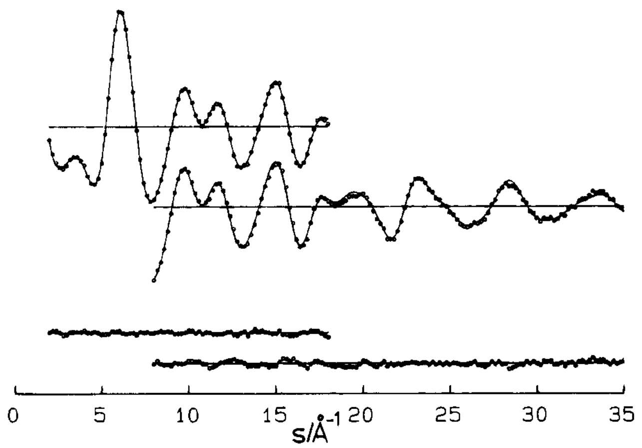

Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for FC(O)OF.

Scheme 1

liquid helium-cooled Si bolometer (Infrared Laboratories) together with a 6 μm Mylar beam splitter was used in the region 550–80 cm^{-1}. In this region, 256 scans were coadded for each spectrum.

Raman spectra of solid FC(O)OF at −196 °C were recorded with a resolution of 2 cm^{-1} on a Bruker FRA 106 FT Raman spectrometer using the 1064 nm exciting line of a narrow-band Nd-YAG laser (ADLAS, DPY 301).

Theoretical Calculations

The geometries of *cis-* and *trans*-FC(O)OF were fully optimized with ab initio methods (HF/3-21G, HF/6-31G*, and MP2/6-31G*) and by local and nonlocal density functional theory methods (LDFT and NLDFT). The ab initio calculations were performed with the GAUSSIAN90 program system,[9] and the LDFT and NLDFT calculations, with the program DGAUSS.[10] Furthermore, the vibrational frequencies of both conformers were calculated at the MP2/6-31G* level (see Tables 1 and 2). The geometric parameters and energy differences $\Delta E = E(cis) - E(trans)$ are included in Table 6.

Vibrational Spectra of the FC(O)OF Isomers

In contrast to the isoelectronic planar fluorine nitrate molecule, O_2NOF,[11] fluoroformyl hypofluorite, FC(O)OF, exists in an equilibrium of two planar conformers (Scheme 1).

In order to distinguish the individual vibrational spectra of the isomers, thermal effusive molecular beams of equilibrium mixtures at different temperatures were trapped in argon matrices. The set of infrared bands which increase in intensity with decreasing temperature belong to the thermodynamically more stable conformer. Also, two sets of bands were observed in the Raman spectrum of solid FC(O)OF deposited at −196 °C from the gas phase at room temperature.

A priori it is not possible to assign the two sets of bands to *cis-* or *trans*-FC(O)OF. This assignment is possible by comparing the observed and calculated gas band contours of both conformers. Using the structural paramenters of the isomers (see below), it can be shown that both are prolate asymmetric rotators ($\chi(cis) = -0.65$, $\chi(trans) = -0.70$). The band contours were calculated using the equations given by Seth-Paul.[12] For A- (PQR), B- (PR), and C-type (PQR) bands of *cis-* and *trans*-FC(O)OF the same $\Delta\nu$(PR) separations of 18.1, 14.4, and 27.2 cm^{-1}, respectively, are expected. Most vibrations of both conformers have the dipole moment vector oscillating not parallel to the axes of inertia, and hybrid band contours are observed. But a nearly pure B-type band contour is expected for the CO-stretching mode of *trans*-FC(O)OF and a nearly pure A-type band for the *cis* conformer. Indeed, the CO-stretching band of the most abundant (stable) conformer shows a PR contour and the same band for the less stable conformer shows a prominent Q-branch. This assignment, that *trans*-FC(O)OF is more stable than *cis*-FC(O)OF, is in accordance with the results of gas electron diffraction, ab initio calculations (see below), and the ^{19}F NMR study.[4]

The assignments of all vibrational bands of *cis-* and *trans*-FC(O)OF, collected in Tables 1 and 2, respectively, are straightforward. For both species, the irreducible representation of the nine fundamentals is as follows:

$$\Gamma_{vib} = 7a'(\mathrm{IR, Ra\ p}) + 2a''(\mathrm{IR, Ra\ dp})$$

The two a″ bands are the out-of-plane deformation (ν_8) and the torsional mode (ν_9).

The infrared gas band of *trans*-FC(O)OF near 740 cm^{-1} shows a contour with a prominent Q-branch progression, which is different from the contours of all other bands. Hence this band is assigned to ν_8. The respective band for *cis*-FC(O)OF was first detected in the matrix and finally found in the gas phase spectrum. The lowest observed band must be the torsional mode ν_9. All further bands are of a′ symmetry and they are assigned by comparison with the band positions from the ab initio calculation. They are collected in Tables 1 and 2 along with several overtones and combinations. The vibrational wavenumbers of ^{18}O-enriched species are also included. Because an equimolar mixture of FC(^{18}O)OF and FC(O)^{18}OF is formed in the synthesis, these frequencies were assigned on the basis of the normal-coordinate analysis.

Determination of the *cis/trans* Equilibrium

As mentioned above, the more stable species is *trans*-FC(O)OF. In order to evaluate the enthalpy and entropy difference, seven matrix spectra of equilibrium mixtures FC(O)OF obtained from beam sources in the temperature range −45 to +140 °C, were analyzed and the entropies for both isomers were calculated from statistical thermodynamics. Very recently, we showed that the gas phase equilibrium is not disturbed by quenching of the molecular beam as a matrix, if the barrier for internal rotation is at least 30–40 kJ mol^{-1}.[5] Since the barrier for the interconversion *cis-* to *trans*-FC(O)OF amounts to 35 kJ mol^{-1}, as derived from NMR experiments,[4] reliable enthalpy differences can be expected from this method. The band pairs for *cis-* and *trans*-FC(O)OF for ν_1, ν_2, ν_4, ν_5, and ν_8 are suitable for determinations of the integrated intensity ratio from the different matrix spectra. Typical matrix spectra in the region of ν_1 and

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Table 1. Observed and Calculated Vibrational Wavenumbers for *cis*-Fluoroformyl Hypofluorite

		Ar matrix						
IR (gas)	contour $\Delta\nu$(PR)	FC(O)OF	int[b]	FC(^{18}O)OF	FC(^{18}O)OF	Raman (solid)	calcd[a]	assgnt
3768.8		3779.8	0.6					$2\nu_1$
2837.0								$\nu_1 + \nu_3$
		2752.2	0.3	2719.2	2719.2			$\nu_1 + \nu_4$
2509.0		2493.7	0.9	2490.9	2476.9			$2\nu_2$
		2174.2	0.6					$\nu_2 + \nu_3$
		2109.0	0.6	2103.7				$\nu_2 + \nu_4$
1905.8	Q	1895.7	91		1890.9	1868 (s)	1960 (330)	ν_1 (a′)
		1865.8	66	1845.2				$\nu_2 + \nu_5$
		1851.3	6.0					$2\nu_3$
1789.3		1781.9	1.3					$\nu_2 + \nu_6$
		1464.9	1.0	1456.7	1461.7			$2\nu_8$
		1458.1	2.4					$\nu_3 + \nu_6$
		1389.1	0.5					$\nu_4 + \nu_6$
1261.0	PQR (15.5)	1253.7	100	1252.0	1245.0	1285 (w)	1311 (326)	ν_2 (a′)
		1245.5	2.0					$2\nu_5$
936.0		929.8	8.8			950 (s)	989 (10)	ν_3 (a′)
861.0	PQR (16.6)	861.1	8	858.2	833.4	871 (vs)	902 (39)	ν_4 (a′)
736.7		733.0	23	728.8	731.0	737 (w)	731 (32)	ν_8 (a″)
626.5	Q	626.3	5.3			634 (m)	630 (18)	ν_5 (a′)
		530.1	0.7			540 (s)	537 (3)	ν_6 (a′)
317.2		315.8	0.5			319 (m)	328 (3)	ν_7 (a′)
150.5		154.1	0.1			119 (w)	138 (0.3)	ν_9 (a″)

[a] Ab initio, MP2/6-31G* level. IR intensities in parentheses in km mol^{-1}. [b] Relative integrated band intensity, Ar matrix.

Table 2. Observed and Calculated Vibrational Wavenumbers for *trans*-Fluoroformyl Hypofluorite

		Ar matrix						
IR (gas)	contour $\Delta\nu$(PR)	FC(O)OF	int[b]	FC(^{18}O)OF	FC(^{18}O)OF	Raman (solid)	calcd[a]	assgnt
3845.0	PR	3826.8	0.7					$2\nu_1$
2920.0		2907.3	0.4	2867.4				$\nu_1 + \nu_3$
2837.0	PR	2827.9	0.2	2788.6	2806.7			$\nu_1 + \nu_4$
2372.0	PR	2351.9	1.7					$2\nu_2$
2175.7	PQR (15.0)	2160.8	0.5	2150.8	2129.9			$\nu_2 + \nu_3$
2096.0	PQR	2083.5	0.6	2073.4	2046.4			$\nu_2 + \nu_4$
		1974.0	5.3	1955.1	1931.6			$2\nu_3$
1932.5	PR (15.4)	1924.5	83	1891.0	1911.7	1905 (s)	1995 (333)	ν_1 (a′)
		1888.9	8.5	1870.2	1836.2			$\nu_3 + \nu_4$
		1829.7	0.3	1819.0	1815.7			$\nu_2 + \nu_5$
1645.4	PQR (18.3)	1639.5	0.5	1621.5	1605.5			$\nu_3 + \nu_5$
		1477.5	0.9	1469.1	1472.4			$2\nu_8$
1413.8	PQR (18.4)	1409.9	0.4	1398.5	1379.0			$\nu_4 + \nu_6$
1310.3	Q	1306.1	0.4	1288.3	1290.8			$2\nu_5$
1216.0	Q	1211.3	2.5	1197.3	1184.3			$\nu_4 + \nu_7$
1191.2	PQR (17.9)	1181.1	100	1179.3	1173.9	1204 (w)	1242 (374)	ν_2 (a′)
		1156.1	0.2	1141.7	1143.3			$\nu_5 + \nu_6$
992.0	PR (15.8)	990.2	10	981.5	963.4	1004 (m)	1038 (20)	ν_3 (a′)
909.7	PQR (18.2)	908.2	11	900.5	880.2	914 (vs)	943 (31)	ν_4 (a′)
742.9	Q	739.1	16	735.0	737.1	737 (w)	735 (30)	ν_8 (a″)
655.2	PQR (16.6)	653.5	3.7	644.1	645.7	661 (s)	655 (8)	ν_5 (a′)
505.1	PQR (15.6)	503.6	0.6	500.4	499.8	511 (s)	511 (2)	ν_6 (a′)
307.1	PQR	304.8	3.6	297.8	303.6	319 (m)	308 (3)	ν_7 (a′)
186.0	Q	193.4	0.2	193.1	187.7	203 (w)	189 (0.03)	ν_9 (a″)

[a] Ab initio, MP2/6-31G* level. IR intensities in parentheses in km mol^{-1}. [b] Relative integrated band intensity, Ar matrix.

ν_2 are shown in Figure 2. Van't Hoff plots of the intensity data for ν_1, ν_2, ν_4, ν_5, ν_8 and linear regressions result in $\Delta H^\circ = H^\circ(cis) - H^\circ(trans)$ values of 4.31, 4.62, 5.42, 4.83, 5.25 kJ mol^{-1}, respectively. As two examples, the linear regressions for ν_1 and ν_2 are shown in Figure 3; deviations are due to uncertainties in band intensity measurements and overlap by bands of dimers. We believe the average value $\Delta H^\circ = 4.9$ kJ mol^{-1} is correct within ± 0.3 kJ mol^{-1}. From rotational constants (derived from the structural parameters) and vibrational wavenumbers (Tables 1 and 2, matrix values) the entropies 314.32 and 312.87 J mol^{-1} K^{-1} are calculated for the *cis* and *trans* conformers, respectively. The difference $\Delta S^\circ = 1.45$ J mol^{-1} K^{-1} is mainly due to the difference in the torsional frequencies which were observed in matrix only. We assume that this value is a good approximation for the gas phase interconversion process. The ab initio calculations at the MP2/6-31G* level confirm this value closely (ΔS°(calc) = 1.80 J mol^{-1} K^{-1}). Using these experimental ΔH° and ΔS° values, the equilibrium composition at 298 K is calculated to be 14% *cis*-FC(O)OF and 86% *trans*-FC(O)OF. These figures are in good agreement with the directly measured equilibrium from NMR experiments (13% *cis*- and 87% *trans*-FC(O)OF).[4]

Force Field Calculation

Normal-coordinate analyses for both conformers were performed to confirm the assignments of bands, to gain some insight into the bonding, and to calculate mean square vibrational amplitudes to be used in the electron diffraction study. The calculation of the force field was carried out with the program NORCOR.[13] A set of nine nonredundant internal coordinates

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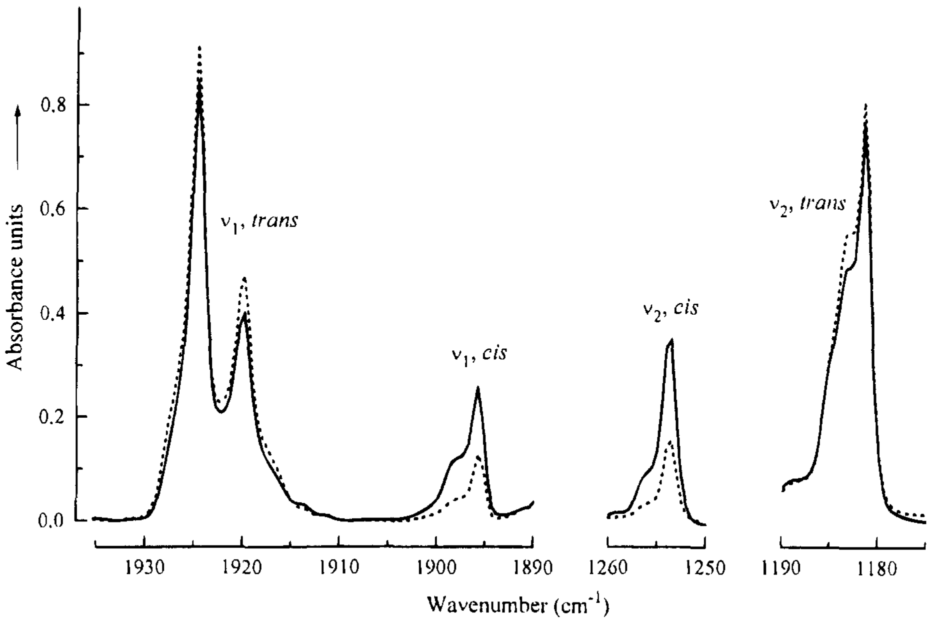

Figure 2. Traces of IR spectra in the region of ν_1 and ν_2 of equilibrium mixtures of *cis*- and *trans*-FC(O)OF held at −45 °C (dots) and +140 °C (full line) quenched in argon matrices.

Table 3. Force Constants (10^2 N m^{-1}) and Potential Energy Distribution (PED) of *cis*-FC(O)OF[a]

	force constants[b]		PED								
	exp	calcd[c]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
f_{rt}	13.95	(15.13)	0.94								
f_{rc}	6.67	(6.88)		0.56	0.23						
f_r	5.81	(5.99)		0.54	0.24	0.31					
f_R	3.46	(4.63)			0.32	0.32		0.31			
f_α	2.81	(2.76)		0.34			1.17	0.18			
f_β	2.01	(2.61)		0.18	0.11	0.17	0.13	0.26	0.84		
f_γ	2.22	(1.79)				0.28	0.19	0.13	0.42		
f_{oop}	0.49	(0.44)								1.01	
f_τ	0.13	(0.11)									1.01
$f_{r\alpha}$	−1.07	(−0.93)		−0.22							
$f_{r\gamma}$	1.13	(0.71)				−0.19					
$f_{\alpha\beta}$	1.44	(1.63)		−0.30		−0.14	−0.47	−0.26	−0.25		
$f_{\alpha\gamma}$	−0.51	(−0.47)					−0.19				

[a] Key: rt, C=O; rc, C−F; r, C−O; R, O−F; α, ∠C(O)F; β, ∠C(O)O; γ, ∠COF; oop, out of plane; τ, torsion about C−O bond. [b] Further force constants contributing less than 0.1 to the PED: $f_{rtrc} = 0.74$ (0.90); $f_{rtr} = 0.96$ (0.89); $f_{rtR} = -0.14$ (−0.02); $f_{rt\alpha} = 0.55$ (0.49); $f_{rt\beta} = 0.83$ (0.58); $f_{rt\gamma} = 0.14$ (0.15); $f_{rcr} = 0.54$ (0.63); $f_{rcR} = 0.82$ (0.05); $f_{rc\alpha} = 0.17$ (−0.03); $f_{rc\beta} = -0.37$ (−0.66); $f_{rc\gamma} = -0.03$ (−0.08); $f_{rR} = 0.30$ (0.24); $f_{r\beta} = -0.17$ (−0.51); $f_{R\alpha} = -0.16$ (0.10); $f_{R\beta} = 0.01$ (0.30); $f_{R\gamma} = 0.44$ (0.38); $f_{\beta\gamma} = -0.01$ (−0.30); $f_{oop\tau} = 0.03$ (−0.21). [c] MP2/6-31G*.

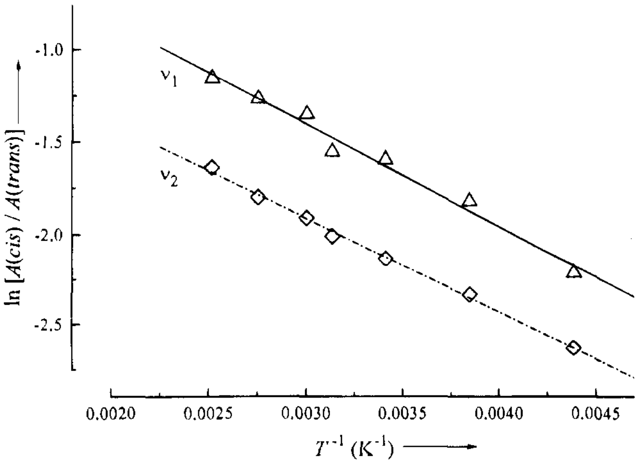

Figure 3. Van't Hoff plots for the equilibrium *cis*-FC(O)OF ⇌ *trans*-FC(O)OF for ν_1 and ν_2 (see text).

were chosen (see Table 3) which are equivalent to the internal coordinates used in the **Z** matrix of the GAUSSIAN 90 program. This allows a direct comparison of the force constants derived from the normal-coordinate analysis with those obtained by the ab initio method. As input data, we used the structural parameters (see below), the frequencies of the matrix fundamentals (Table 1 and 2), and, as starting solutions, the force field from ab initio calculations (Tables 3 and 4). In the first step, only diagonal force constants were fitted. With these preliminary results, vibrational wavenumbers of ^{18}O-substituted molecules were calculated, compared with the observed ones, and finally assigned (see Tables 1 and 2). By using the product rule for the a″ vibrations, it was possible to confirm the assignments discussed above. In the final refinement of the 31 force constants in internal coordinates of *cis*- and *trans*-FC(O)OF all independent vibrational data, 16 and 21, respectively, were used. Force constants which were less sensitive to vibrational wavenumbers of different isotopomers were fixed close to the ab initio values. Except for ν_1 and ν_2, where the band positions are disturbed by anharmonic resonances with combination bands, it was possible to reproduce the vibrational data given in Tables 1 and 2 within experimental uncertainties with the final force fields presented in Tables 3 and 4. The force field, calculated for *cis*-FC(O)OF, is less reliable because insufficient vibrational data were available for the fit. The potential energy distribution shows that ν_1, ν_8, and ν_9 are characteristic vibrations, i.e. the C=O stretching, out-of-plane

Table 4. Force Constants (10^2 N m^{-1}) and Potential Energy Distribution (PED) of *trans*-FC(O)OF[a]

	force constants[b]		PED								
	exp	calcd[c]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
f_{rc}	14.46	(15.41)	0.95								
f_{rt}	6.15	(6.68)		0.64	0.16		0.21				
f_r	5.76	(5.97)		0.38	0.35	0.31					
f_R	4.44	(4.98)			0.35	0.55					
f_α	2.50	(2.53)		0.38			0.62	0.44			
f_β	2.61	(2.47)		0.48			0.55		0.58		
f_γ	1.51	(1.63)				0.16	0.14		0.71		
f_{oop}	0.51	(0.29)								1.02	
f_τ	0.20	(0.20)									0.99
f_{rtr}	0.87	(0.78)		−0.14							
$f_{rt\beta}$	−0.89	(−0.88)		−0.24			0.15				
$f_{r\alpha}$	−0.50	(−0.56)		−0.10							
$f_{r\gamma}$	0.81	(0.52)				−0.12					
$f_{\alpha\beta}$	1.45	(0.46)		−0.49			−0.67	0.16	−0.23		

[a] Key: rc, C=O; rt, C−F; r, C−O; R, O−F; α, ∠C(O)F; β, ∠C(O)O; γ, ∠COF; oop, out of plane; τ, torsion about C−O bond. [b] Further force constants contributing less than 0.1 to the PED: $f_{rcrt} = 0.90$ (0.88); $f_{rcr} = 0.82$ (0.77); $f_{rcR} = 0.02$ (0.02); $f_{rc\alpha} = 0.60$ (0.53); $f_{rc\beta} = 0.52$ (0.50); $f_{rc\gamma} = -0.16$ (0.11); $f_{rtR} = 0.07$ (0.02); $f_{rt\alpha} = -0.27$ (0.31); $f_{rt\gamma} = -0.12$ (−0.16); $f_{rR} = 0.05$ (0.08); $f_{r\beta} = 0.44$ (0.07); $f_{R\alpha} = -0.28$ (0.19); $f_{R\beta} = -0.51$ (0.33); $f_{R\gamma} = 0.29$ (0.51); $f_{\alpha\gamma} = -0.03$ (−0.19); $f_{\beta\gamma} = 0.02$ (0.07); $f_{oop\tau} = -0.05$ (−0.05). [c] MP2/6-31G*.

bending, and torsional modes, respectively. All further vibrations are strongly coupled.

As expected, the CO and CF force constants are similar to those in FC(O)F (CO, 14.88; CF, 6.77 10^2 N m^{-1}).[14] It is interesting to note that in both conformers the bond which lies trans to O−F is weakened: in *trans*-FC(O)OF the C−F bond is weaker than that in *cis*-FC(O)OF and the opposite is true for the C=O bonds. These trends are confirmed by the calculated bond lengths (see Table 6). The unexpected large difference between the OF force constants in both isomers may be an artifact.

Gas Electron Diffraction Analysis

The radial distribution function (RDF) for FC(O)OF is shown in Figure 4. The calculated RDF's for the pure *trans* and *cis* conformers differ in the region around 2.6 Å. Comparison with the experimental curve demonstrates that the major component must be the *trans* conformer. In the least-squares analysis the molecular intensities were modified with a diagonal weight matrix[8] and known scattering amplitudes and phases were used.[15]

Since all theoretical calculations result in planar structures for this molecule, the geometry is fully described by seven geometric parameters (four bond distances and three bond angles). Vibrational amplitudes were collected in groups according to their distances. Since some interatomic distances are closely spaced in this molecule and their vibrational amplitudes cause large correlations between parameters, all but two amplitudes were constrained to the values derived from the normal-coordinate analysis. Nevertheless, large correlations between geometric parameters still occur in the least-squares refinement (Table 5).

A considerable improvement of the fit of the experimental intensities is obtained by including a small contribution of the *cis* conformer. The agreement factor for the long camera distance, R_{50}, decreases from 0.048 to 0.039 for 18% *cis*. The differences in bond lengths and angles between the *cis* and in the *trans* forms were constrained to the respective ab initio values (MP2/6-31G*). For all parameters these differences are small, except for the O=C−O and C−O−F angles, which differ by ca. 10 and 4°, respectively, in the *trans* and *cis* forms. The ratio of the *trans* and *cis* conformers is not well determined in the GED experiment (18 ± 12% *cis*) and was fixed to the

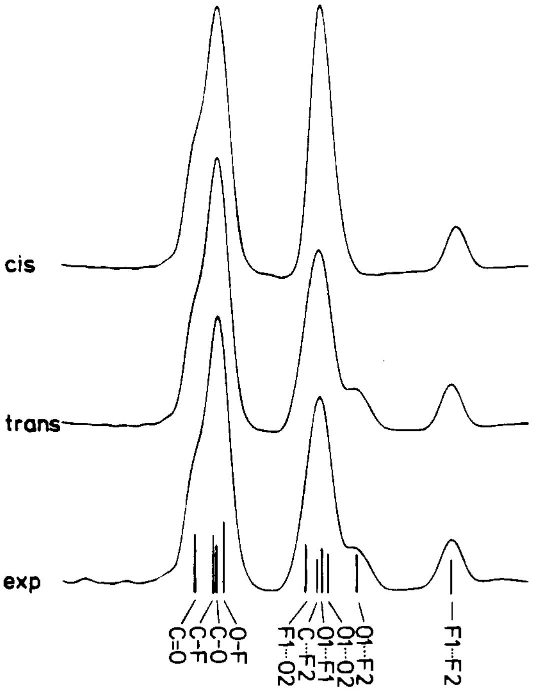

Figure 4. Calculated radial distribution function for *cis* and *trans* conformers, experimental curve, and difference for FC(O)OF (for atom numbering see Figure 5).

Table 5. Correlation Coefficient (×100) for FC(O)OF

C=O	100								
C−F	64	100							
C−O	−62	−91	100						
O−F	56	79	−85	100					
O=C−F	−65	−77	75	−69	100				
O=C−O	51	77	−71	66	−90	100			
C−O−F	−44	−56	43	−52	35	−36	100		
a(C=O)	−21	−25	32	−24	23	−20	9	100	
$a(F_1 \cdots F_2)$	0	0	−1	0	0	−1	−3	0	100

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Table 6. Geometric Parameters for FC(O)OF[a]

	GED[b]		HF/3-21G	HF/6-31G*	MP2/6-31G*	LDFT[c] TZVP	NLDFT[d] TZVP
	trans	*cis*	*trans*	*trans*	*trans*	*trans*	*trans*
C=O	1.170(4)	1.172	1.170	1.157	1.186	1.180	1.188
C−F	1.324(7)	1.320	1.326	1.295	1.335	1.328	1.351
C−O	1.367(9)	1.380	1.379	1.341	1.372	1.355	1.377
O−F	1.418(5)	1.425	1.426	1.357	1.435	1.407	1.445
O=C−F	126.5(6)	126.4	126.3	126.4	127.2	127.3	127.0
O=C−O	130.3(6)	120.9	129.2	129.0	130.3	130.3	131.3
C−O−F	105.5(4)	109.6	106.6	108.0	105.4	106.7	107.0
ΔH° [e]/ΔE	4.9(3)		7.24	8.16	6.78	−2.09	−3.35
%	86	14					

[a] Distances in angstroms and angles in degrees. [b] Error limits are 3σ values. Differences between the parameters of *trans* and *cis* conformer are taken from the MP2/6-31G* calculation. [c] Local density functional theory.[16] [d] Nonlocal density functional theory, exchange functional of Becke[17] and correlation functional of Perdew.[18] [e] $\Delta H^\circ = \Delta H^\circ(cis) - \Delta H^\circ(trans)$ (kJ mol^{-1}) from matrix IR spectra, $\Delta E = \Delta E(cis) - \Delta E(trans)$ (kJ mol^{-1}) from theoretical calculations.

Table 7. Interatomic Distances and Vibrational Amplitudes a_k from Electron Diffraction and Spectroscopic Data[a]

	trans			cis		
	dist	*a*(GED)	*a*(spectr)	dist	*a*(GED)	*a*(spectr)
C=O	1.170	0.042(4)	0.036	1.172	0.042[b]	0.036
$C-F_1$	1.324	0.046[b]	0.045	1.320	0.046[b]	0.043
$C-O_2$	1.367		0.047	1.380		0.047
O_2-F_2	1.418		0.046	1.425		0.050
$O_1\cdots F_1$	2.229	0.051[b]	0.051	2.226	0.052[b]	0.050
$O_1\cdots O_2$	2.304		0.051	2.223		0.056
$O_1\cdots F_2$	2.547	0.094[b]	0.094	3.401	0.057[b]	0.057
$F_1\cdots O_2$	2.109	0.060[b]	0.058	2.248	0.057[b]	0.057
$C\cdots F_2$	2.217		0.062	2.292		0.059
$F_1\cdots F_2$	3.354	0.066(7)	0.060	2.371	0.089[b]	0.089

[a] Values in Å angstroms; error limits are 3σ values. For atom numbering see Figure 5. [b] Not refined.

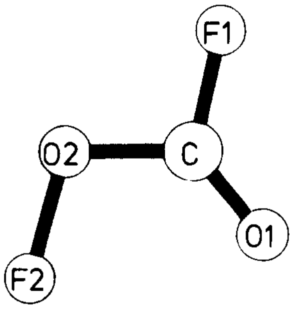

Figure 5. Atom numbering for FC(O)OF.

spectroscopic value in the final refinement (14%; see above). The final results are presented in Table 6 (geometric parameters) and Table 7 (vibrational amplitudes).

Results and Discussion

The most interesting aspects of this study are the conformational properties of FC(O)OF. All experiments demonstrate clearly that the *trans* conformer is the prevailing one with a small contribution of the *cis* conformer. The conformational ratio is well determined by spectroscopy. Independent of the computational method, all theoretical calculations confirm the existence of two stable structures, planar *trans* and planar *cis*. The energy difference, however, strongly depends on the computational method (see Table 6). A strict comparison between the experimental ΔH° and the calculated ΔE values requires inclusion of differences in zero-point vibrational energies and thermal contributions between the two conformers. According to the MP2/6-31G* calculations, ΔH° and ΔE differ by 0.55 kJ mol^{-1}, such that the calculated ΔE values have to be increased by this difference for comparison with the experiment. All three ab initio calculations predict the *trans* conformer to be the more stable one, in agreement with the experiment, but the energy difference is overestimated. The local and nonlocal density functional theory calculations, however, predict a slight preference for the *cis* form, which is in disagreement with the experiment.

Comparison of FC(O)OF with formic acid, HC(O)OH, shows that fluorination has a considerable effect on the conformational properties. In both compounds, the *trans* form with the O−F and O−H bonds eclipsing the C=O double bond is preferred, but the energy difference between *trans* and *cis* conformers decreases from 16.33(36) kJ mol^{-1} in HC(O)OH[19] to 4.9(3) kJ mol^{-1} in FC(O)OF. The conformational properties of the partially fluorinated derivative, fluoroformic acid, FC(O)OH, are not yet accessible by experiments. Theoretical calculations also predict for this molecule the *trans* form to be more stable by 6−12 kJ mol^{-1}, depending on the calculational method.[20,21]

The calculated bond distances for FC(O)OF show the well-known trends, i.e. shortening with increasing basis set and lengthening with inclusion of electron correlation. Both, HF/3-21G and MP2/6-31G* methods reproduce the experimental values very well. The HF/6-31G* method predicts all bond distances too short, especially the O−F bond (by 0.06 Å). Also the LDFT method gives good agreement with the experiment, somewhat better than the NLDFT method. Bond angles depend little on the computational method and are close to the experimental values.

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Supplementary Material Available: Tables giving total electron diffraction intensities and backgrounds (4 pages). Ordering information is given on any current masthead page.

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