Inorg. Chem. **1998,** *37,* 6208−6213

IR and UV Absorption Cross Sections, Vibrational Analysis, and the Molecular Structure of Trifluoromethyl Peroxynitrate, CF_3OONO_2

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Received July 7, 1998

The synthesis of CF_3OONO_2 is accomplished by UV photolysis (254 nm) of a mixture of CF_3I, NO_2, and O_2. The pure product is isolated after trap-to-trap condensation. The removal of byproducts is accomplished by treatment of the crude product with O_3. To complement the known physical and spectroscopical properties of CF_3OONO_2, the IR and UV absorption cross sections are determined, and a complete vibrational analysis is performed. On the basis of the UV data, the photolytic half-life in the troposphere is calculated to be 30 days. The molecular structure of CF_3OONO_2 is determined by gas-phase electron diffraction and quantum chemical calculations (HF/3-21G, HF/6-31G*, and B3PW91/6-311+G*). The peroxide CF_3OONO_2 possesses a skew structure (C_1 symmetry) with a COON dihedral angle of 105.1(16)° and an extremely long O−N bond of 1.523(7) Å, which is in accordance with its low O−N bond-dissociation energy. The HF/3-21G and B3PW91/6-311+G* methods reproduce the experimental geometry satisfactorily whereas the HF/3-31G* approximation predicts a much shorter O−N (1.390 Å).

Introduction

The most advantageous property of CFC replacements is their ability to be degraded in the troposphere by attack via OH radicals. The fluorinated organic radicals formed in this manner are rapidly converted by reaction with molecular oxygen into peroxy radicals.[1] The currently used alternatives to CFC's, such as CF_3H, CF_3CH_3, CF_3CHClF, CF_3CHCl_2, etc., contain a CF_3 moiety that may be converted into CF_3OO radicals in the atmosphere.[2−9] These radicals can react with themselves or, more likely, with other atmospheric radicals. The reaction with NO_2 in which trifluoromethyl peroxynitrate is formed is important in this regard. CF_3OONO_2 may serve as a reservoir molecule for either $CF_3O_{1,2}$ or NO_2 radicals, which may contribute to the depletion of ozone in the stratosphere or to the transport of NO_2 from industrial zones into otherwise pollution-free environments.[2,9]

In the laboratory, CF_3OONO_2 was first synthesized by DesMarteau and co-workers[10] in the reaction of CF_3OOH with N_2O_5 or CF_3OOF with N_2O_4. In addition, it was synthesized in situ in smog chambers by the photolysis of CF_3NO or CF_3I in the presence of O_2 and NO_2.[11−13]

Because of the difficulties in performing the synthesis,[10] the compound is still incompletely characterized. CF_3OONO_2 is a colorless liquid with a boiling point of 0.9 °C. Its mass, IR, Raman, and ^{19}F NMR spectra have been recorded.[10] Recently, the thermal decomposition of CF_3OONO_2 was investigated.[9,11]

$$CF_3OO + NO_2 + M \rightleftharpoons CF_3OONO_2 + M \qquad (1)$$

From the temperature dependence of the kinetics of formation and decomposition, the CF_3OO-NO_2 bond enthalpy was deduced to be 102.7 ± 2 kJ mol^{-1}.[9,11] Therefore the atmospheric thermal lifetime at low altitudes is short, but in the tropospause, it may be about 1 year.[9,11] The atmospheric photochemical lifetime can be calculated from the absorption cross sections for wavelengths >290 nm. However, the UV spectrum of CF_3OONO_2 is unknown.

In earlier studies of CFO containing compounds of atmospheric relevance, we have reported the synthesis and characterization of $FC(O)OONO_2$[14] and $CF_3C(O)OONO_2$.[15] The results of an improved synthesis, an extensive characterization,

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10.1021/ic980776p CCC: $15.00

and an electron-diffraction study of CF_3OONO_2 are reported in this study.

Experimental Section

Caution! Trifluoromethyl peroxynitrate and especially ozone are potentially explosive. It is important to take the appropriate safety precautions when these compounds are handled in the liquid or solid state. Reactions involving these compounds should be carried out only with millimolar quantities.

General Procedures and Reagents. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-1000, MKS Baratron, Burlington, MA) and valves with PTFE stems (Young, London). The vacuum line was connected to an IR cell (optical pass length 200 mm, Si windows 0.5-mm thick) in the sample compartment of the FTIR instrument.

For Raman measurements, the sample was transferred into a 2-mm glass capillary. NMR measurements were carried out on samples in flame-sealed, 5-mm-o.d. tubes, which were centered inside a 10 mm tube containing $CDCl_3$ (Merck) and $CFCl_3$ (Merck) as lock and reference.

Details of the matrix-isolation apparatus and the conditions for preparing noble gas matrixes have been given elsewhere.[16] The products were stored in flame-sealed glass ampules in liquid nitrogen. The ampules were opened and resealed by use of an ampule key.[17]

Synthesis of CF_3OONO_2. A 5-L photoreactor equipped with a water-cooled, 15-W low-pressure mercury lamp was connected to the vacuum line, loaded with 55 mbar of CF_3I and 40 mbar of NO_2, and filled with oxygen up to 1 atm. The vacuum line was connected to an IR cell in the sample compartment of a Nicolet FTIR spectrometer in order to observe the reaction process. The photolysis was accomplished at 0 °C. Every 30 min, a small amount of the gas mixture was analyzed by IR spectroscopy. The highest concentration of CF_3OONO_2 was detected after about 2 h. Because of the similar vapor pressures of CF_3OONO_2 and CF_3I,[18] it was impossible to separate the compounds by trap-to-trap condensation.Therefore, the photolysis of the gas mixture was continued until all CF_3I was depleted (about 5 h). The concentrations of the decomposition products (F_2CO, FNO_x) increased during this process. Subsequently the gas mixture was passed through three traps immersed in liquid nitrogen, and the collected crude product was separated by repeated trap-to-trap condensation in vacuo in a series of traps held at −100, −120, and −196 °C, respectively. The trap at −120 °C retained CF_3OONO_2 contaminated with NO_2. To remove the NO_2 impurities, batches of about 0.5 mmol of the crude product were condensed into a 250-mL vessel and equal amounts of ozone were condensed onto it. The vessel was allowed to warm to room temperature, and the mixture was separated in the same manner as described above. N_2O_5 was retained in the −100 °C trap, and the −120 °C trap contained pure CF_3OONO_2. No impurities were detectable in the IR, ^{19}F NMR, and ^{13}C NMR spectra. The yield of CF_3OONO_2 amounted to 30−70% (2.5−5.5 mmol, based on NO_2), depending on the conditioning of the inner surface of the photoreactor.

Instrumentation. (A) Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000−400 cm^{-1}, using a FTIR instrument (Nicolet Impact 400 D). In the range 450−80 cm^{-1}, a Bruker IFS 66v FTIR instrument fitted with a gas cell (20-cm optical path length) equipped with polyethylene windows was used. The same instrument was used for recording matrix infrared spectra in the range 4000−400 cm^{-1}, with a resolution of 1 cm^{-1}.

FT Raman spectra of a liquid sample were recorded with a Bruker FRA 106 FT Raman accessory mounted on the optical bench of the IFS 66v instrument. The 1064-nm exciting line of a Nd:YAG laser (ADLAS, DPY 301, Lübeck, Germany) was used.

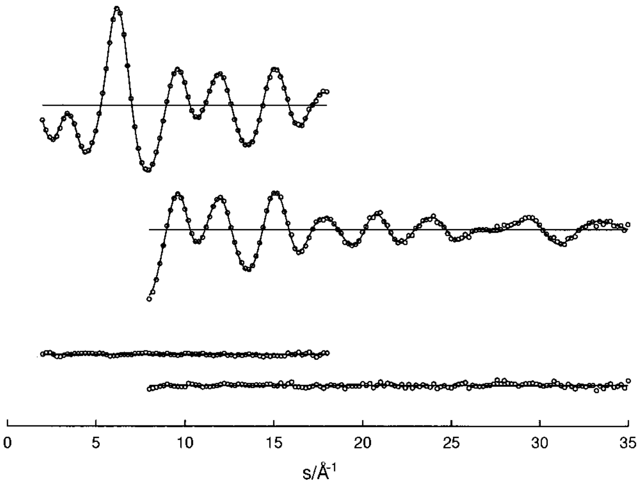

Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for long (upper curves) and short (lower curves) nozzle-to-plate distances.

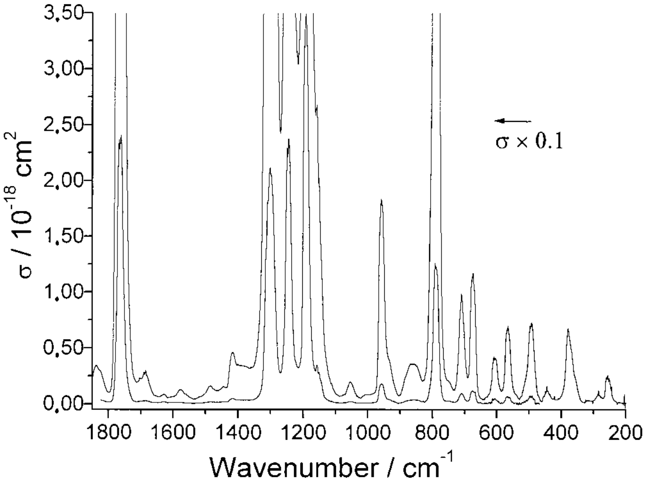

Figure 2. IR spectra of CF_3OONO_2 in the gas phase.

(B) NMR Spectroscopy. The ^{19}F and ^{13}C NMR spectra of the neat liquid sample were recorded with a Bruker MSL 200 spectrometer and a $^{19}F/^{1}H$ dual head (for ^{19}F) or a multinuclear probe head (for ^{13}C), operating at 188.31 and 50.33 MHz, respectively. For each ^{19}F NMR spectrum of the sample, four scans were accumulated in a 64-kB memory, with a delay time of 2.2 s between scans. For the ^{13}C NMR spectrum, 132 scans of the same sample were recorded with a delay time of 60 s. Low-temperature measurements were carried out by using a Bruker variable-temperature controller with a copper−constantan thermocouple.

(C) UV Spectroscopy. UV spectra in the 190−290 nm region were recorded with a 1024 diode array spectrometer (Spectroscopy International). A CLD 30-W deuterium lamp (Hamamatsu) was employed as the light source. Mercury emission lines from penray lamps (Oriel) were used for wavelength calibrations. To eliminate absorption from atmospheric oxygen, the monochromator and the housing of the absorption cell were flushed with nitrogen. Spectra in the 250−340-nm region were recorded with a Lamda 900 (Perkin-Elmer) spectrometer. The gas-phase UV spectrum of CF_3OONO_2 was recorded by using a glass cell (100-mm optical path length) equipped with quartz lenses (Suprasil, Heraeus) or by using quartz cells (50-mm optical path length, Suprasil, Hellma). Pressures were measured with a capacitance manometer (100 or 1000 mbar absolute; 122 A, MKS Baraton, Burlington, MA).

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$$CF_3I\text{:}\ \log(p) = 7.5665 - 1174.29/T$$

$$CF_3OONO_2\text{:}\ \log(p) = 7.567 - 1284.4/T \qquad (10)$$

Table 1. Wavenumbers (cm^{-1}) of the Vibrational Bands of CF_3OONO_2 and Their Assignments

IR						
gas	σ^a	Ar matrix	I^b	Raman liquid	ab initio[c]	assignm/approx description of mode[d]
3505	0.91	3522	2.9			$2\nu_1$
3056	6.00	3052	2.3			$\nu_1 + \nu_3$
2611	1.40	2606	0.2			$2\nu_2$
2588	0.90	2567	0.2			$2\nu_3$
2482	1.25	2465	0.9			$2\nu_4$
2375	0.80	2367	0.2			$2\nu_5$
2122	1.32	2116	0.3			$\nu_5 + \nu_6$
2071	1.25	2068	0.3			$\nu_3 + \nu_8$
1986	1.06					$\nu_1 + 4\nu_{20} - \nu_{20}$
1838	3.36					$\nu_1 + 2\nu_{20} - \nu_{20}$
1762(P)	241	1762	71	1759(1)	1811 (354)	ν_1 $\nu_{as}(NO_2)$
1576	2.90					$2\nu_8$
1415	4.55	1418	1.2	1415(0.5)		$2\nu_9$
1314 sh	139	1308	40		1335 (220)	ν_2 $\nu_s(NO_2)$
1303	210	1290	70	1308(5)	1277 (288)	ν_3 $\nu_s(CF_3)$
1244(P)	238	1238	100	1235(<0.5)	1227 (316)	ν_4 $\nu_{as}(CF_3)$
1192	349	1187	79	1179(1)	1150 (526)	ν_5 $\nu_{as}(CF_3)$
1054	1.96					$\nu_8 + \nu_{18}$
958	17.7	960 br	13	955(2)	970 (43.5)	ν_6 $\nu(O-O)$
860 br	3.5	880 br	4.1	881(9)	854 (1.8)	ν_7 $\nu(C-O)$
792	126	787	38	785(3)	814 (189)	ν_8 $\delta(NO_2)$
710	9.6	708	3.4	700(<0.5)	733 (16.6)	ν_9 $\delta_{oop}(NO_2)$
					715 (1.1)	ν_{10} $\delta_s(CF_3)$
674	11.3	676	3.6	673(2)	684 (15.3)	ν_{11} $\delta_{as}(CF_3)$
608	4.37	609	1.8	604(<0.5)	605 (7.5)	ν_{12} $\delta_{as}(CF_3)$
565	6.85	570	2.8	565(4)	576 (10.6)	ν_{13} $\rho(NO_2)$
495	6.96	498	3.4	492(7)	483 (9.5)	ν_{14} $\nu(N-OO)$
445	1.35	450	4.9	445(3)	444 (0.64)	ν_{15} $\rho(CF_3)$
380	6.8			367(7)	375 (7.0)	ν_{16} $\rho(CF_3)$
286	1.2			287(2)	287 (1.2)	ν_{17} $\delta(OO-NO_2)$
256	2.6			257(10)	261 (1.0)	ν_{18} $\delta(OO-CF_3)$
~180 br	~0.1			190(<0.5)		$2\nu_{20}$
					103 (0.002)	ν_{19} $\tau(F_3CO-ONO_2)$
				94(10)	85 (0.089)	ν_{20} $\tau(F_3COO-NO_2)$
					60 (0.008)	ν_{21} $\tau(F_3C-OONO_2)$

[a] Absorption cross section in 10^{-20} cm^2. [b] Rel. integrated intensities; $I(\nu_4) \equiv 100$. [c] B3PW91/6-31G*, wavenumbers of the stretching modes are scaled by a factor of 0.95; values in parentheses are IR intensities in km mol^{-1}. [d] ν = stretching, δ = deformation, oop = out of plane, ρ = rocking, and τ = torsion.

(D) Gas Electron Diffraction (GED). Electron-diffraction intensities were recorded with a Gasdiffraktograph KD-G2[19] at 25- and 50-cm nozzle-to-plate distances and an accelerating voltage of ca. 60 kV. The sample reservoir was kept at −70 °C (ca. 15-mbar vapor pressure), and the inlet system and gas nozzle were at room temperature. The photographic plates (Kodak electron image plates, 13 × 18 cm) were analyzed by the usual methods.[20] Averaged molecular intensities in the *s* ranges of 2−18 and 8−35 Å^{-1} (in steps of $\Delta s = 0.2$ Å^{-1}) are shown in Figure 1.

Results and Discussion

Synthesis of CF_3OONO_2. According to the literature,[9] the synthesis of CF_3OONO_2 is accomplished by the reaction of photolytically generated CF_3 radicals with O_2 and NO_2 in a modified procedure.

In the first step, CF_3 radicals are formed in situ by

$$CF_3I \xrightarrow{h\nu} CF_3 + I \qquad (2)$$

In the presence of oxygen the CF_3 radicals add O_2 to form CF_3OO.[21,22]

$$CF_3 + O_2 \rightarrow CF_3OO \qquad (3)$$

The resulting radical may now react with a second CF_3OO molecule (eq 4), CF_3 (eq 5), or NO_2 (eq 1).

$$CF_3OO + CF_3OO \rightarrow CF_3OOCF_3 + O_2 \qquad (4)$$

$$CF_3OO + CF_3 \rightarrow CF_3OOCF_3 \qquad (5)$$

$$CF_3OO + NO_2 + M \rightleftharpoons CF_3OONO_2 + M \qquad (1)$$

Because of the low concentrations of CF_3 and CF_3OO radicals, reaction (1) occurs preferentially. The photolytic cleavage of NO_2 takes place as a side reaction.

$$NO_2 \rightarrow NO + O \qquad (6)$$

Nitrogen monoxide depletes the product,[9,21]

$$CF_3OONO_2 \rightleftharpoons CF_3OO + NO_2 \qquad (1)$$

$$CF_3OO + NO \rightarrow CF_3O + NO_2 \qquad (7)$$

$$CF_3O + NO_x \rightarrow CF_2O + FNO_x \qquad (8)$$

and CF_2O, FNO, and FNO_2 are found in the crude product.

During the handling of the pure substance, very small amounts of NO_2 are formed. This is in accordance with its thermal instability at room temperature.[9,11]

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Table 2. Selected IR Absorption Cross Sections of Gaseous CF_3OONO_2

mode	position/cm^{-1}	$\sigma/10^{-20}$ cm^2 this work	ref 9	ref 12
$\nu_{as}(NO_2)$	1762(P)/1768(R)	241/237	−/90	69
$\nu_s(CF_3)$	1303	210	68	61
$\nu_{as}(CF_3)$	1244(P)/1250(R)	238/229	71/70	110
$\nu_{as}(CF_3)$	1192	349	100	130
$\nu(O-O)$	958	17.7	5.83	24
$\delta(NO_2)$	792	126	23	37

Table 3. UV Absorption Cross Section of Gaseous CF_3OONO_2 at 28 °C[a]

λ/nm	$\sigma/10^{-20}$ cm^2	λ/nm	$\sigma/10^{-20}$ cm^2
185	430	265	8.2(0.3)
190	370	270	5.8(0.2)
195	290	275	4.0(0.2)
200	220	280	2.6(0.1)
205	150	285	1.7(0.1)
210	96(7)	290	1.0(0.05)
215	74(4)	295	0.69
220	54(4)	300	0.45
225	46(3)	305	0.28
230	38(2)	310	0.20
235	32(2)	315	0.13
240	27(1)	320	0.08
245	22(1)	325	0.05
250	18.0(0.7)	330	0.037
255	14.3(0.6)	335	0.024
260	11.1(0.5)	340	0.014

[a] Values in brackets are $n - 1$ standard deviations of 5−10 measurements.

Table 4. Experimental and Calculated Geometric Parameters for CF_3OONO_2

	GED[a]	HF/ 3-21G[b]	HF/ 6-31G*[b]	B3PW91/ 6-311+G*[b]
O−O	1.414(8)	1.441	1.364	1.394
O−N	1.523(7)	1.494	1.390	1.538
O−C	1.378 [12][c]	1.393	1.372	1.392
N=O	1.187(3)	1.205	1.169	1.179
C−F	1.322(3)	1.327	1.302	1.325
O−O−N	108.4(13)	107.1	110.6	109.1
O−O−C	107.7(14)	107.6	108.7	108.7
O=N=O	135.2(21)	133.6	131.8	135.2
ΔONO = (O2−N=O4) − (O2−N=O3)	7.9[d]	7.6	8.2	7.9
F−C−F	108.8(9)	109.7	109.7	109.4
tilt (CF_3)[e]	4.6[d]	3.7	3.9	4.6
ϕ(C−O−O−N)	105.1(16)	104.7	106.2	104.5
ϕ(O−O−N=O3)	178.3[d]	173.4	176.7	178.3
ϕ(O−O−C−F1)	181.8[d]	185.0	182.0	181.8

[a] r_a values are in angstroms and degrees. Error limits are 3σ values and include possible systematic errors (see text). For atom numbering, see Figure 3. [b] Mean values are given for parameters which are not unique. [c] Not refined but varied within the range given in brackets (for estimations of possible systematic errors). [d] Not refined. [e] Tilt between the C_3 axis of the CF_3 group and the O−C bond direction. The tilt is away from the O−O bond.

Spectroscopic Properties. (A) Vibrational Spectra. Figure 2 shows the gas-phase infrared spectrum of CF_3OONO_2. For quantitative analysis, the ordinate scale is presented in the absorption cross section, and selected values at all band centers are collected in Table 1. The cross sections are determined according to

$$\sigma = 31.79T \log I_0/I \times (pd)^{-1}/10^{-20}\ \text{cm}^2 \qquad (9)$$

with T = temperature (Kelvin), p = pressure (mbar), and d = optical path length (cm).

CF_3OONO_2 possesses C_1 symmetry (vide infra), and all 21 fundamentals are expected to be active in the infrared and Raman spectra. They can be subdivided into 8 stretching, 10 deformation, and 3 torsional modes. Altogether, 20 fundamentals are detected in the IR and Raman spectra. Of these, 19 are found in the infrared spectrum and 19 in the Raman spectrum. The torsional mode of lowest energy [$\tau(CF_3-O)$] is missing, because it is expected to appear outside the range of our spectrometers.

All vibrational data observed in the gas phase, in an argon matrix, and for the pure liquid are listed together with the calculated wavenumbers (ab initio) and a tentative assignment in Table 1. The observed band positions are, within a few wavenumbers, in general agreement with the literature values.[10] However, the assignment given by Hohorst and DesMarteau is based on C_s symmetry, and four fundamentals were not observed in their spectra. Our assignment is based on a comparison with the spectra of $CF_3C(O)F$,[23] $FC(O)OONO_2$,[14] and $CF_3C(O)OONO_2$.[15] All stretching modes at high wavenumbers are characteristic and easily assignable, except for the $\nu_s(CF_3)$ and $\nu_s(NO_2)$ fundamentals (ν_3 and ν_2, respectively), which overlap strongly in the infrared gas spectrum. The assignment of ν_2 and ν_3 is based on the results of the ab initio calculation. The skeletal bending modes are strongly mixed, and the proposed assignment is arbitrary.

For comparison, literature values of the absorption cross sections[9,12] of $\nu_{as}(NO_2)$, $\nu_s(CF_3)$, $\nu_{as}(CF_3)$, $\nu(OO)$, and $\delta(NO_2)$ are listed in Table 2. Because the literature data are deduced from complex reaction mixtures, their absolute and relative values are strongly affected by overlapping bands of impurities.

(B) UV Spectra. In the UV region, gaseous CF_3OONO_2 shows an absorption ranging from 340 nm with increasing intensity toward 190 nm. The absorption cross sections listed in Table 3 are obtained from several samples at pressures between 0.5 and 807 mbar. At high pressures, the characteristic absorption pattern of NO_2 appears. The spectrum recorded with a pressure of 807 mbar shows an absorption of 0.07 at 380 nm. By comparison with a pure NO_2 sample, this absorption corresponds to a partial pressure of ca. 1 mbar of NO_2. Therefore, the raw spectra are corrected by subtracting the respective NO_2 content.

The UV spectrum of CF_3OONO_2 is similar in shape to the spectrum of CH_3OONO_2;[24] however, CF_3OONO_2 has absorption cross sections lower than those of CH_3OONO_2 by a factor of about 2.

From the absorption cross sections, the photolytic half-life for CF_3OONO_2 in the troposphere is calculated using the solar flux data of Zepp and Cline and Zepp's GCSOLAR program[25] (sea level, Greenwich meridian, all latitudes, unity quantum yield). A half-life of about 26 days is derived. For the northern hemisphere mid-latitudes, a half-life of about 30 days is calculated using the data of Frank and Klöpffer.[26] These values are higher than those reported in the literature,[9,11] which were

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Table 5. Interatomic Distances and Vibrational Amplitudes[a]

	distance	ampl GED		ampl HF/3-21G		distance	ampl GED		ampl HF/3-21G
N═O	1.19	0.039 [b]		0.039	F2··O4	2.99	0.199(39)	l_4	0.159
C−F	1.32	0.043(3)	l_1	0.043	N··F2	3.03	0.199(39)	l_4	0.161
O−C	1.38	0.047[b]		0.047	C··N	3.19	0.108[b]		0.108
O−O	1.41	0.045[b]		0.045	C··O4	3.28	0.199(39)	l_4	0.162
O−N	1.52	0.054[b]		0.054	O2··F1	3.39	0.061[b]		0.061
F··F	2.15	0.060(6)	l_2	0.057	O1··O3	3.41	0.063[b]		0.063
O3··O4	2.18	0.047[b]		0.047	F2··O3	3.89	0.216(44)	l_5	0.225
O2··O3	2.21	0.060(6)	l_2	0.061	N··F3	3.90	0.216(44)	l_5	0.205
O1··F	2.15−2.24	0.060(6)	l_2	0.058	F1··O4	4.02	0.216(44)	l_5	0.237
O2··C	2.26	0.067[b]		0.067	C··O3	4.13	0.144(33)	l_6	0.133
O2··O4	2.32	0.060(6)	l_2	0.057	N··F1	3.22	0.144(33)	l_6	0.143
O1··N	2.38	0.065[b]		0.065	F3··O4	4.30	0.256[b]		0.256
O1··O4	2.53	0.091[b]		0.091	F3··O3	4.60	0.275[b]		0.275
O2··F2	2.66	0.129(19)	l_3	0.142	F1··O3	5.28	0.136[b]		0.136

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

derived from comparison with $CCl_xF_{3-x}OONO_2$[24] or from preliminary UV data.[27] On the basis of our data, CF_3OONO_2 may play a more important role than previously expected in the transport of NO_2 from industrial zones into pollution-free environments.

(C) NMR Spectra. In the ^{19}F NMR spectrum of a liquid CF_3OONO_2 sample of high purity at −30 °C, only one signal at −71.4 ppm relative to $CFCl_3$ is observed. The coupling constant $^1J_{CF}$ determined from the positions of the ^{13}C satellites is 269.5 Hz. The ^{13}C NMR spectrum of the same sample at −30 °C shows one quartet at 123.7 ppm relative to TMS and a $^1J_{CF}$ coupling constant of 269.5 Hz as observed in the ^{19}F NMR spectrum.

It is interesting to note that the isoelectronic compound $CF_3OOC(O)F$[28] shows very similiar data for the CF_3 group (liquid, −50 °C, $\delta_F = -71.8$ ppm, $\delta_C = 122.3$ ppm, $^1J_{CF} = 269.5$ Hz).[29]

(D) Gas-Phase Structure. The structure of CF_3OONO_2 is determined by theoretical methods, as well as by GED. Geometric parameters are fully optimized with the HF/3-21G, HF/6-31G*, and B3PW91/6-311+G* methods.[30] These results are included in Table 4. Cartesian force constants (HF/3-21G) are transformed to symmetry constants, and vibrational amplitudes are calculated with the program ASYM40[31] (Table 5). Stretching and bending constants are scaled with 0.85 and torsional constants with 1.0.

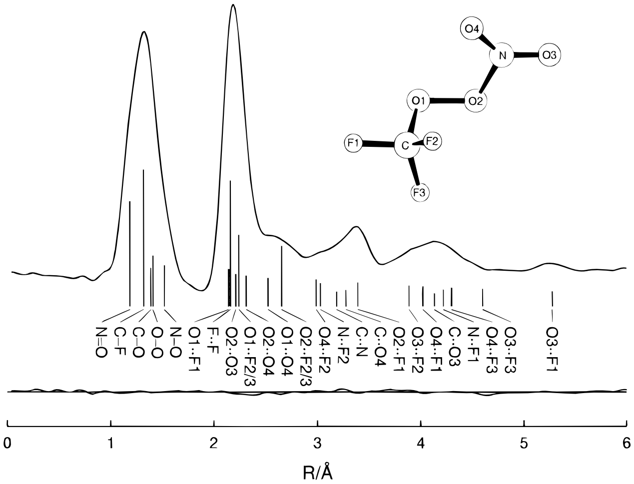

Figure 3. Experimental radial distribution function and difference curve. The positions of interatomic distances are shown by vertical bars.

The experimental radial distribution function (RDF) is calculated by Fourier transformation of the GED intensities (Figure 3). A preliminary structural model derived from the RDF is refined by least-squares fitting of the molecular intensities. A diagonal weight matrix is applied to the intensities, and known complex scattering factors are used.[32] Because CF_3OONO_2 possesses some very similar bond distances which cause high correlations in the least-squares analysis, the O−C bond length is constrained to the value derived for CF_3OOOCF_3 [1.378(12) Å].[33] The bond length is varied within its uncertainty of ±0.012 Å for estimating possible systematic errors in refined parameters caused by this constraint. The CF_3 group is assumed to possess C_{3v} symmetry, the tilt angle between the C_3 axis and the O−C bond direction, and the torsional angle ϕ(OOCF1) are fixed at the calculated values. The ONO_2 group is constrained to planarity, the difference between the two O−N═O angles $\Delta ONO = (O2{-}N{=}O4) - (O2{-}N{=}O3)$, and the torsional angle ϕ(OONO3) is constrained to the B3PW91 values (for atom numbering, see Figure 3). The bond lengths N═O3 and N═O4 are set equal. The calculated difference (B3PW91) is only 0.003 Å. Vibrational amplitudes for similar interatomic distances are collected in groups, and amplitudes which cause high correlations or which are badly determined in the GED experiment are set to the ab initio values (see Table 5). Through the use of these constraints, nine geometric parameters and six vibrational amplitudes are refined simultaneously. The following correlation coefficients have values larger than |0.5|: CF/

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OOC = −0.52, CF/FCF = 0.63, OOC/FCF = −0.63, OO/l_1 = −0.64, FCF/l_2 = −0.87. The final results are listed in Tables 4 (geometric parameters) and 5 (vibrational amplitudes l_k).

CF_3OONO_2 possesses a skew structure with C_1 symmetry and a COON dihedral angle of 105.1(16)°. This angle is intermediate between those for CF_3OOCF_3 [ϕ(COOC) = 123.3(40)°][34] and for FC(O)$OONO_2$ [ϕ(COON) = 86.2(14)°].[14] This comparison indicates that sp^2-hybridized substituents, such as FC(O) or NO_2, tend to decrease the dihedral angle in peroxides. Within the experimental uncertainties, the O−O bond length in CF_3OONO_2 [1.414(8) Å] is equal to those in CF_3OOCF_3 [1.419(20) Å] and FC(O)$OONO_2$ [1.420(6) Å]. These bonds in peroxides with electronegative substituents are shorter than those in hydrogen peroxide [1.475(4) Å][35] or dimethyl peroxide [1.457(12) Å].[36] The most remarkable structural feature of CF_3OONO_2 is the extremely long O−N bond of 1.523(7) Å. Structural studies of covalent nitrates $XONO_2$ have shown that the N−O single bond length depends strongly on the electronegativity of the substituent X. For the electropositive $SiMe_3$ group, a very short N−O bond of 1.383(5) Å is observed.[37] The bond length increases with increasing electronegativity to 1.410(2) Å in $HONO_2$,[38] 1.493(3) Å in $ClONO_2$,[39] and 1.507(4) Å in $FONO_2$.[40] The result for CF_3OONO_2 suggests that the CF_3O group is even more electron withdrawing than fluorine.

Both methods, low-level HF/3-21G and high-level B3PW91/6-311+G*, reproduce the refined experimental geometric parameters satisfactorily, i.e., to within ±0.03 Å and ±3°. The HF/6-31G* approximation predicts O−N and O−O bond lengths which are too short by 0.13 and 0.05 Å, respectively. All three methods predict COON dihedral angles which are indistinguishable from the experimental value.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

IC980776P