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Properties of Azidotrifluoromethane

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The infrared spectrum of gaseous and the Raman spectrum of liquid CF_3N_3 were recorded. A total of 14 fundamental vibrations out of 15, expected for a model of symmetry C_s with hindered rotation, were observed and assigned. The UV, ^{19}F NMR, and mass spectra were also recorded and confirm the presence of a covalent azido group. The melting point and vapor pressure curve of CF_3N_3 are reported.

Introduction

Although the existence of CF_3N_3 has been known for almost 2 decades,[1] very little is known about this interesting molecule. In 1961 Makarov and co-workers mentioned[1] that CF_3N_3 is formed during the chlorination of CF_3NNNH_2, and in 1968 they described its synthesis in more detail.[2] However, the compound was only characterized by elemental analysis, its boiling point, and a statement concerning its explosive properties at elevated temperature.[2] No further information on CF_3N_3 could be found in the literature. This is not surprising in view of the explosive character generally exhibited by covalent azides.[3,4] In view of this paucity of data, a characterization of CF_3N_3 was carried out, the results of which are summarized in this paper.

Experimental Section

Caution! Although no explosions were encountered in this study, covalent azides are in general explosive,[3,4] and Makarov and co-workers reported that CF_3N_3 explodes at 330 °C.[2] Consequently, appropriate safety precautions should be taken when working with larger amounts of CF_3N_3.

Materials and Apparatus. Volatile materials were manipulated in a stainless-steel vacuum line equipped with Teflon FEP U traps and 316 stainless-steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Gas chromatographic data were obtained with use of a Varian GC under isothermal conditions with a stainless-steel column ($^1/_8$ in. × 10 ft) packed with Poropak PS. Trifluoronitrosomethane (PCR Research Chemicals, Inc.) and hydrazine (Olin-Mathieson) were used as received.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer using a Teflon cell of 5-cm path length equipped with CsI windows. The spectrometer was calibrated by comparison with standard gas calibration points,[5,6] and the reported frequencies are believed to be accurate to $\pm 2\ cm^{-1}$.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser and a Claassen filter[7] for the elimination of plasma lines. Quartz tubes (4-mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described[8] device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.[7]

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the $CFCl_3$ solvent with positive shifts being downfield from $CFCl_3$.[9]

The mass spectra were recorded with an EAI Quad 300 quadrupole spectrometer at an ionization potential of 40 eV.

The UV spectra were recorded on Cary Model 14 spectrophotometer using a stainless-steel cell of 10-cm path length equipped with sapphire windows.

Synthesis of CF_3N_3. A 200-mL glass ampule containing a stirring bar was loaded with 78.1 mmol of N_2H_4 and 40 mL of CH_3OH, stirred and cooled to −78 °C. After removal of air, CF_3NO (83 mmol) was bled into the cooled ampule during 2.5 h resulting in a blue-green solution. Trifluoronitrosomethane in the vapor phase was removed, and Cl_2 was added (78 mmol during 2 h) to the stirred −78 °C solution giving a light yellow liquid phase. The solution was allowed to warm slowly, and the gas generated was passed through a coarse glass frit, NaOH scrubber. In 4 h approximately 76 mmol of crude CF_3N_3 passed the scrubber. Final purification was effected by fractional condensation through traps cooled at −78, −126, −142, and −196 °C. The −196 °C fraction was mainly CF_3NO while the −78 °C trap contained traces of material which was discarded without examination. The remaining traps contained the colorless CF_3N_3 (70 mmol, 89% yield on the basis of N_2H_4 taken) whose GC indicated purity was 98–99%. Storage in stainless-steel cylinders for several weeks at ambient temperature at several atmospheres pressure did not result in any significant decomposition.

Results and Discussion

Synthesis and Properties of CF_3N_3. For the synthesis of CF_3N_3 the procedure of Makarov and coworkers[2] was followed. It involves reactions 1 and 2.

$$CF_3NO + H_2NNH_2 \rightarrow CF_3N{=}NNH_2 + H_2O \quad (1)$$

$$CF_3N{=}NNH_2 + Cl_2 \rightarrow CF_3N_3 + 2HCl \quad (2)$$

Azidotrifluoromethane is white as a solid and colorless as a liquid and a gas. It melts at −152 °C. It is stable at room temperature and can be handled without noticeable decomposition. Vapor pressures were measured over the range −95 to −45 °C, and the data were fitted by the method of least squares to eq 3 with an index of correlation of 0.9998. The

$$\log P\ (\mathrm{mm}) = 7.8748 - 1221.7/T\ (\mathrm{K}) \quad (3)$$

extrapolated boiling point is −28.5 °C, in good agreement with that of −28.5 °C at 743 mm, previously reported.[2] Measured vapor pressures at the noted temperatures are as follows (T, °C, P, mm): −95.2, 10; −78.6, 40; −64.6, 108; −45.5, 324. The latent heat of vaporization of CF_3N_3 is 5.591 kcal/mol, and the derived Trouton constant is 22.9, indicating little association in the liquid phase.

Vibrational Spectra. Figure 1 shows the infrared spectrum of gaseous and the Raman spectrum of liquid CF_3N_3. The observed frequencies are listed in Table I. By analogy with the known structures of CH_3N_3,[10,11] CF_3OF,[12,13] and ClN_3,[14]

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[1] Makarov, S. P.; Yakubovich, A. Ya.; Ginsburg, V. A.; Filatov, A. S.; Englin, M. A.; Privezentseva, N. F.; Nikiforova, T. Ya. *Dokl. Akad. Nauk SSSR*, **1961**, *141*, 357.

[2] Makarov, S. P.; Yakubovich, A. Ya.; Filatov, A. S.; Englin, M. A.; Nikiforova, T. Ya. *Zh. Obshch. Khim.*, **1968**, *38*, 709.

[3] "The Chemistry of the Azido Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1971.

[4] Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 240.

[5] Plyler, E. K.; Danti, A.; Blaine, L. R.; Tidwell, E. D. *J. Res. Natl. Bur. Stand., Sect. A*, **1960**, *64*, 841.

[6] International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers"; Butterworths: Washington, D.C.; 1961.

[7] Claassen, H. H.; Selig, H.; Shamir, J. *Appl. Spectrosc.* **1969**, *23*, 8.

[8] Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1970**, *24*, 271.

[9] *Pure Appl. Chem.* **1972**, *11*, 1215.

[10] Livingston, R. L; Rao, C. N. R. *J. Phys. Chem.* **1960**, *64*, 756.

[11] Salathiel, W. M.; Curl, R. F., Jr., *J. Chem. Phys.* **1966**, *44*, 1288.

[12] Buckley, P.; Weber, J. P. *Can. J. Chem.* **1974**, *52*, 942.

[13] Diodati, F. P; Bartell, L. S. *J. Mol. Struct.* **1971**, *8*, 395.

[14] Cook, R. L.; Gerry, M. C. L. *J. Chem. Phys.* **1970**, *53*, 2525.

0020-1669/81/1320-2566$01.25/0

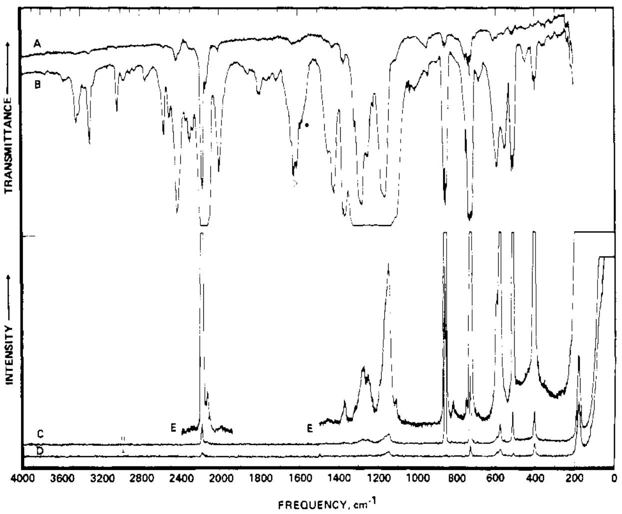
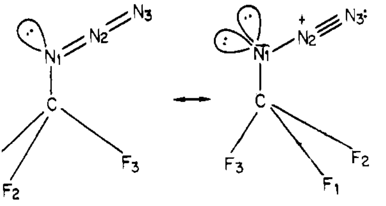


Figure 1. Vibrational spectra of CF_3N_3. Traces A and B: infrared spectra of the gas recorded in a 5-cm path length cell equipped with CsI windows at pressures of 8 and 255 mm, respectively. The bands marked by a diamond and an asterisk are believed to be due to an impurity and CF_3NO, respectively. Traces C–E: Raman spectra of the liquid, recorded at −100 °C at two different sensitivities and with the incident polarization parallel and perpendicular.

the CF_3N_3 molecule is expected to possess a structure of symmetry C_s with a planar CN_3 backbone, an approximately linear N_3 group, a staggered CF_3 group, and $r_{N_1N_2}$ (~1.25 Å) being significantly longer than $r_{N_2N_3}$ (~1.13 Å) due to II being the most important resonance structure. Structure I would be analogous to that of $CF_3N{=}O$[15] in which the CF_3 and NO group are eclipsed. Whether the CF_3 is eclipsed or staggered depends on the coordination number of N_1, including its sterically active valence electron pairs as ligands. If N_1 is three-coordinated, as in CF_3NO or structure I, the highly repulsive free valence electron pair of N_1 will avoid the fluorine ligands of the CF_3 group and therefore cause the free valence electron pair of N_1 to be staggered and the N=X ligand to be eclipsed relative to the CF_3 group. However, if N_1 is four-coordinated, as in II, the two free valence electron pairs on N_1 and the N–X group should all be staggered with respect to the CF_3 group.



I II

Assuming hindered rotation of the CF_3 group, CF_3N_3 should exhibit 15 fundamental modes of vibration, all active in both the infrared and the Raman spectra. Of these, 10 belong to species a′ and can be either polarized or depolarized, while 5 belong to species a″ and should be depolarized in the Raman spectrum. An approximate description of these 15 fundamental vibrations is given in Table II. Eight of them involve motions of the CF_3 group, four are due to the N_3 group, and three involve the C–N linkage.

Assignments for the four N_3 modes were made by comparison with the known spectra of the covalent azides, FN_3[16], ClN_3,[16,17] BrN_3,[16] IN_3,[18] CH_3N_3,[19-22] CD_3N_3,[21,22] HN_3,[23-27] DN_3,[23-27] and OPF_2N_3[28] (see Table II). Of the four N_3 modes, two are due to stretching motions, one antisymmetric and one symmetric. Since the two NN bonds significantly differ in their bond strength, the higher frequency mode might equally well be described as mainly a stretching of the N_2N_3 bond and the lower one as mainly a stretching of the N_1N_2 bond; however, due to the linear N_3 structure, both modes should be strongly coupled.[22] On the basis of its high frequency and relative intensity, the N_2N_3 stretch is readily assignable to the

Table I. Vibrational Spectra of CF_3N_3

obsd freq, cm⁻¹, and intens[a]		
IR (gas)	Raman (liquid)	assignt in point group C_s
3465 w		$\nu_1 + \nu_2 = 3466$ (a′)
3436 sh		$\nu_1 + \nu_3 = 3436$ (a′)
3327 w		$\nu_1 + \nu_4 = 3332$ (a′)
3039 w		$\nu_1 + \nu_5 = 3041$ (a′)
2755 vw		$\nu_1 + \nu_7 = 2762$ (a′)
2567 w		$2\nu_2 = 2568$ (a′)
2510 w		$2\nu_3 = 2508$ (a′)
2440 mw		$\nu_2 + \nu_4 = 2434$ (a′)
2410 sh		$\nu_3 + \nu_4 = 2404$ (a′)
2354 vw		$\nu_1 + \nu_{10} = 2361$ (a′)
2302 vw		$2\nu_4 = 2300$ (a′)
2270 vw		
2183 s	2182 (1.1) p	ν_1 (a′)
2140 m	2137 (0.1)	$\nu_2 + \nu_5 = 2143$ (a′)
2018 mw		$\nu_2 + \nu_6 = 2014$ (a′)
1856 vw		$\nu_2 + \nu_7 = 1864$ (a′)
1798 w		$\nu_2 + \nu_8 = 1797$ (a′)
1713 vw		$2\nu_5 = 1718$ (a′)
1629 mw		} impurity?
1613 mw		
1590 w		$\nu_5 + \nu_6 = 1589$ (a′) or CF_3NO?
1455 w		$2\nu_6 = 1460$ (a′)
1427 mw		$\nu_3 + \nu_{10} = 1432$ (a′)
1370 mw	1370 (0.1)	$\nu_5 + \nu_8 = 1372$ (a′)
1316 m		$\nu_6 + \nu_7 = 1310$ (a′)
1284 vs, PQR	1280 } (0.2) p	ν_2 (a′)
1255 ms	1253	ν_3 (a′)
1223 mw		C_2F_6 impurity?
1169 vs	1165 sh, dp?	ν_{11} (a″)
1152 sh	1149 (0.5) p	ν_4 (a′)
1110 sh	1110 (0+)	C_2F_6 impurity or $2\nu_{13} = 1112$ (a′)?
1034 vw		$\nu_5 + \nu_{10} = 1038$ (a′)
1009 vw		
859 mw, PQR	859 (10) p	ν_5 (a′)
	814 (0+)	?
751 w, PQR	751 (0+)	$\nu_7 + \nu_{10} = 759$ (a′)
731 m, PQR	730 (3.8) p	ν_6 (a′)
687 vw	685 (0+)	$\nu_8 + \nu_{10} = 692$ (a′)
594 mw	594 (0.2) dp	ν_{12} (a″)
582 sh	580 (1.1) p	ν_7 (a′)
557 w	555 sh	ν_{13} (a″)
513 mw, PQR	514 (1.7) p	ν_8 (a′)
450 vw		ν_{14} (a″)
402 w, PQR	403 (1.6) p	ν_9 (a′)
	179 (4.3) p	ν_{10} (a′)

[a] Uncorrected Raman intensities representing relative peak height.

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(15) Davis, M. I.; Boggs, J. E.; Coffey, D., Jr.; Hanson, H. P. *J. Phys. Chem.* **1965**, *69*, 3727. Turner, H. P.; Cox, P. A. *Chem. Phys. Lett.* **1976**, *19*, 585.
(16) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1964**, *40*, 2461.
(17) Clark, T. C.; Clyne, M. A. A. *Trans. Faraday Soc.* **1969**, *65*, 2994.
(18) Dehnicke, K. *Angew. Chem.* **1976**, *88*, 612.
(19) Fateley, W. G.; Miller, F. A. *Spectrochim. Acta* **1961**, *17*, 857.
(20) Manica, E.; Zerbi, G. *Gazz. Chim. Ital.* **1960**, *90*, 53.
(21) Miller, F. A.; Bassi, D. *Spectrochim. Acta* **1963**, *19*, 565.
(22) Thompson, W. T.; Fletcher, W. H. *Spectrochim. Acta* **1966**, *22*, 1907.
(23) Dows, D. A.; Pimentel, G. C. *J. Chem. Phys.* **1955**, *23*, 1258.
(24) Pimentel, G. C.; Charles, S. W.; Rosengren, Kj. *J. Chem. Phys.* **1966**, *44*, 3029.
(25) Moore, G. B.; Rosengren, Kj. *J. Chem. Phys.* **1966**, *44*, 4108.
(26) Levine, D. M.; Dows, D. A. *J. Chem. Phys.* **1967**, *46*, 1168.
(27) Shimanouchi, T. *J. Phys. Chem. Ref. Data*, **1972**, *1*, 202.
(28) O'Neill, S. R.; Shreeve, J. M. *Inorg. Chem.* **1972**, *11*, 1629.

Table II. Assignment of the 15 Fundamental Vibrations of CF_3N_3 Compared to Those of Closely Related Molecules

assignt		approx description of mode for CF_3N_3	obsd freq, cm^{-1}											
			CF_3N_3	CF_3NO^a	CF_3COOH^b	$FN_3{}^c$	$ClN_3{}^c$	$BrN_3{}^c$	$IN_3{}^d$	$CH_3N_3{}^e$	$CD_3N_3{}^e$	$HN_3{}^f$	$DN_3{}^f$	$OPF_2N_3{}^g$
a′	ν_1	$\nu_{as}(N_3)$ or $\nu(N_2N_3)$	2182			2034	2066	2062	2058	2106	2118	2140	2112	2175
	ν_2	$\nu_s(CF_3)$	1284	1291	1254									
	ν_3	$\nu_{as}(CF_3)$	1254	1230	1211									
	ν_4	$\nu_s(N_3)$ or $\nu(N_1N_2)$	1150			1086	1144	1160	1176	1272	1285	1151	1184	1265
	ν_5	$\nu(C-N)$	859	809						910	830			
	ν_6	$\delta_s(CF_3)$	730	730	781									
	ν_7	$\delta(N_3)$ in plane	580			503	520	530	578	666	640	534	492	
	ν_8	$\delta_{as}(CF_3)$	513	533	508									
	ν_9	$\delta_{rock}(CF_3)$	402	428										
	ν_{10}	$\delta(CNN)$	179	296						245	231			
a″	ν_{11}	$\nu_{as}(CF_3)$	1168	1175	1189									
	ν_{12}	$\delta(N_3)$ out of plane	594							560	560	607	588	
	ν_{13}	$\delta_{as}(CF_3)$	556	551	591									
	ν_{14}	$\delta_{rock}(CF_3)$	450	428										
	ν_{15}	τ		[50][h]						126	90			

[a] Data from ref 29 and 30 with some revised assignments. [b] Data from ref 32. [c] Data from ref 16. [d] Data from ref 18. [e] Data from ref 12–22. [f] Data from ref 27. [g] Data from ref 28. [h] Estimated value from ref 29.

band at about 2180 cm^{-1}. The N_1N_2 stretch should occur in the frequency range between 1090 and 1270 cm^{-1} and most likely be of higher Raman intensity than the CF_3 stretching modes. It is therefore assigned to the Raman band at about 1150 cm^{-1}. This assignment agrees well with those reported for ClN_3,[16] BrN_3[16] and IN_3[18] for which this mode occurs at 1144, 1160, and 1176 cm^{-1}, respectively.

The in plane (a′) and out of plane (a″) N_3 deformation modes should occur in the 500–660-cm^{-1} range (see Table II). Two polarized Raman bands were observed in this range at 580 and 514 cm^{-1}, respectively, and must be due to the in plane N_3 deformation and the antisymmetric a′ CF_3 deformation mode. Based on the similarity of the frequencies of the CF_3 modes in CF_3N_3 and CF_3NO[29,30] (see Table II), we prefer to assign the 580-cm^{-1} fundamental to the N_3 a′ deformation and the 514-cm^{-1} one to the CF_3 a′ deformation mode. A similar choice exists for the two corresponding a″ modes for which two bands at 594 and 556 cm^{-1} are available for assignment. By comparison with the related compounds listed in Table II and based on intensity arguments, we prefer to assign 594 cm^{-1} to $\delta(N_3)$ (a″) and 556 cm^{-1} to $\delta_{as}(CF_3)$ (a″). Spectra of ^{15}N-substituted CF_3N_3 would be required to confirm these assignments.

The assignment of the three fundamental vibrations involving mainly the C–N linkage presents no difficulties because they occur at frequencies outside of the ranges expected for the CF_3 and N_3 modes. Thus, the C–N stretching mode obviously[22] must be assigned to the strongest Raman band at 859 cm^{-1}, and the second strongest Raman band at 179 cm^{-1} must be due to the CNN angle deformation. The latter mode was observed[22] at 245 and 231 cm^{-1} for CH_3N_3 and CD_3N_3, respectively, and the further mass increase of the methyl group in CF_3N_3 can account for the observed additional frequency decrease. The C–N torsional modes in CH_3N_3 and CD_3N_3 have frequencies of 126 and 90 cm^{-1}, respectively.[19] On the basis of the larger mass of the CF_3 group, this mode should show again a frequency decrease for CF_3N_3 and should occur well below 90 cm^{-1}. Due to its low frequency, this mode could not experimentally be observed in the present study.

Assignments for a CF_3 group with hindered rotation (C_s symmetry) are generally difficult; however, several recent thorough studies of the vibrational spectra of CF_3X type compounds such as CF_3COX,[31,32] CF_3NO,[29,30] and CF_3OF[33-37] have provided valuable information and permit assignments for most of the CF_3 modes.

As previously pointed out by Redington,[32] the CF_3 modes of molecules of symmetry C_s can be related to those of molecules of symmetry C_{3v}, for which the assignments are well established. Such a correlation is shown in Table III for CF_3N_3, CF_3NO,[29,30] CF_3COOH,[32] CF_3CN,[38] CF_3CCH,[38] and CF_3H.[39] Under C_s symmetry the doubly degenerate e modes of C_{3v} split into one a′ and one a″ component. Although the degree of splitting can significantly vary from compound to compound, the average of the a′ and the a″ frequency is similar

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(29) Shurvell, H. F.; Dass, S. C.; Gordon, R. D. *Can. J. Chem.* **1974**, *52*, 3149.
(30) Demuth, R.; Bürger, H.; Pawelke, G.; Willner, H. *Spectrochim. Acta, Part A* **1978**, *34A*, 113.
(31) Berney, C. V. *Spectrochim. Acta, Part A* **1971**, *27A*, 663.
(32) Redington, R. L *Spectrochim. Acta, Part A* **1975**, *31A*, 1699.
(33) Wilt, P. M. Dissertation, Vanderbilt University, 1967.
(34) Wilt, P. M.; Jones, E. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2108.
(35) Smardzewski, R. R.; Fox, W. B. *J. Fluorine Chem.* **1975**, *6*, 417; *J. Phys. Chem.* **1975**, *79*, 219.
(36) Kuo, J. C.; DesMarteau, D. D.; Fateley, W. G.; Hammaker, R. M.; Marsden, C. J.; Witt, J. D. *J. Raman Spectrosc.* **1980**, *9*, 230. Wahi, P. K.; Patel, N. D. *Can. J. Spectrosc.* **1980**, *25*, 70.
(37) Hammaker, R. M.; Fately, W. G.; Manocha, A. S.; DesMarteau, D. D.; Streusand, B. J.; Durig, J. R. *J. Raman Spectrosc.* **1980**, *9*, 181.
(38) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1973**, *2*, 247 and 250.
(39) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1972**, *1*, 54.

Table III. Spectral Correlation between the Fundamental Vibrations of the CF$_3$ Group in Molecules of Symmetry C_s and Those of Symmetry C_{3v}

C_{3v}					C_s				
		obsd freq, cm^{-1}			obsd freq, cm^{-1}				
class	description of mode	CF$_3$CN[a]	CF$_3$CCH[a]	CF$_3$H[b]	CF$_3$COOH[c]	CF$_3$N$_3$[d]	CF$_3$NO	class	description of mode
a$_1$	ν_s(CF$_3$)	1227[e]	1253[e]	1117	1254	1284	1291	a′	ν_s(CF$_3$)
	δ_s(CF$_3$) (umbrella)	522[e]	536[e]	700	781	730p	730	a′	δ_s(CF$_3$)
e	ν_{as}(CF$_3$)	1214	1179	1152	1211	1254	1230	a′	ν_{as}(CF$_3$)
					1200	1211	1203	[f]	
					1189	1168dp	1175	a″	ν_{as}(CF$_3$)
	δ_{as}(CF$_3$) (scissor)	618	612	507	591	556	551	a″	δ_{as}(CF$_3$)
					549	535	542	[f]	
					508	513p	533	a′	δ_{as}(CF$_3$)
	δ_{rock}(CF$_3$)	463	453		434	450	428	a″	δ_{rock}(CF$_3$)
						402p		a′	δ_{rock}(CF$_3$)

[a] Data from ref 38. [b] Data from ref 39. [c] Data from ref 32. [d] p and dp indicate polarization in the Raman spectra. In C_s symmetry, a″ modes cannot be polarized. [e] Strongly coupled modes (see text). [f] Average frequency of a′ + a″.

to that of the corresponding degenerate e mode. However, the following secondary effects which can influence the frequencies must be kept in mind: (i) the covalency, and thereby the bond strength and frequency values, of the C–F bonds in CF$_3$X increases with increasing electronegativity of X, and (ii) coupling between certain modes can result in large frequency shifts. The tendency for strong coupling is particularly pronounced in the a′ block, when the symmetric CF$_3$ stretching, the C–X stretching, and the symmetric CF$_3$ deformation strongly mix with each other.

In CF$_3$N$_3$, the corresponding three fundamentals occur at 1284, 859, and 730 cm^{-1} and are readily identified by their PQR band contours (parallel bands of an approximate accidental spherical top molecule) and highly polarized Raman bands. On the basis of our experience with related molecules and the observed infrared and Raman intensities, the 1284-cm^{-1} fundamental might be described as an antisymmetric combination of the symmetry coordinates of ν_s(CF$_3$) and those of ν(C–N), the 859-cm^{-1} fundamental as a symmetric combination of the same symmetry coordinates with some contribution from δ_s(CF$_3$), and the 730-cm^{-1} fundamental as mainly a symmetric combination of the symmetry coordinates of the ν(C–N) and δ_s(CF$_3$). Due to this pronounced mixing, arguments concerning the identity of these modes are not very meaningful. It should be kept in mind, however, that, particularly in the a′ block of CF$_3$X type molecules, the above described coupling can cause the frequencies of ν_s(CF$_3$) and δ_s(CF$_3$) to move apart, resulting in an unexpected high frequency for ν_s(CF$_3$) and a low one for δ_s(CF$_3$). This in turn may result for different CF$_3$X type compounds in a different sequence of the a′ and a″ fundamentals and is one of the prrincipal reasons for the existing confusion concerning the proper assignment of CF$_3$ group fundamental vibrations. The coupling between ν_s(CF$_3$) and δ_s(CF$_3$) in a′ of a CF$_3$X type molecule is enhanced when the C–X stretch has a frequency intermediate between those of ν_s(CF$_3$) and δ_s(CF$_3$), and in these cases great care should be exercised when the CF$_3$ fundamentals are assigned.

For CF$_3$N$_3$, the following CF$_3$ modes can be assigned with reasonable confidence. The three CF$_3$ stretching modes are expected to occur in the 1150——1300-cm^{-1} region and therefore are assigned to the fundamental vibrations at about 1168, 1254, and 1284 cm^{-1}. Since the two higher frequency bands are definitely polarized in the Raman spectrum, the 1168-cm^{-1} band must represent the antisymmetric CF$_3$ stretch of species a″, in good agreement with previous conclusions.[31,32,40] On the basis of its PQR infrared band contour, its higher Raman intensity and a comparison with similar molecules,[31,32,40] the highest frequency fundamental vibration is assigned to ν_s(CF$_3$) (a′). On the basis of analogous arguments, the 730-cm^{-1} fundamental vibration must be assigned to the symmetric CF$_3$ deformation of species a′. Adopting the above assignments for the two N$_3$ deformation modes, the antisymmetric CF$_3$ deformation modes are ascribed to the 556- and 513-cm^{-1} bands with the Raman polarization data unambiguously distinquishing the a′ from the a″ mode. The CF$_3$N$_3$ assignments also suggest that in Redington's[32] and Berney's[31] previous studies the assignments of the δ_{as}(CF$_3$) (a′), and δ_{as}(CF$_3$) (a″) might need to be interchanged. Although intensity arguments were cited against such an exchange, it is supported by Raman polarization data.[31,32]

The two modes which in most studies could be assigned only with difficulties are the a′ and a″ CF$_3$ rocking modes. As can be seen from Table III, the corresponding degenerate e mode of symmetry C_{3v} occurs at about 460 cm^{-1}. Therefore, the polarized Raman band, generally observed for CF$_3$X compounds of symmetry C_s in the range 400–430 cm^{-1} should represent the a′ CF$_3$ rocking mode. Since the a″ CF$_3$ rocking mode must be depolarized in the Raman spectrum, the 179-cm^{-1} fundamental vibration of CF$_3$N$_3$ cannot be assigned to this mode. The only vibration left for a possible assignment to the a″ CF$_3$ rocking mode is the weak infrared band at 450 cm^{-1}, unless a coincidence of the symmetric and of the antisymmetric CF$_3$ rocking mode is assumed at 403 cm^{-1}, which would leave no plausible assignment for the 450-cm^{-1} band.

A normal coordinate analysis was not carried out because of the grossly underdetermined nature of the problem and the strong coupling experienced by us and others[30,36] for CF$_3$X type species. Since the force constants and the resulting potential energy distributions can be varied over a wide range with exact reproduction of the observed frequencies, PED-based conclusions concerning the identities of certain fundamental vibrations should be treated with the necessary scepticism.

Numerous overtones and combination bands were observed in the infrared spectrum at higher sample pressures. Almost all of them could be readily assigned (see Table I) and confirm the proposed assignments. The only detectable impurities were possibly traces of C$_2$F$_6$ and CF$_3$NO.

^{19}F NMR Spectrum. The ^{19}F NMR spectrum of CF$_3$N$_3$ was recorded at 27 °C in CFCl$_3$ solution. It consisted of a sharp singlet at −57.6 ppm, upfield from internal CFCl$_3$, characteristic for a CF$_3$ group with all three fluorines being equivalent on a NMR time scale. This is not surprising in view of the relatively low barrier to internal rotation expected[19,29,37] for a molecule such as CF$_3$N$_3$.

Mass Spectrum. The mass spectrum of CF$_3$N$_3$ is listed in Table IV. It shows a strong parent ion at m/e 111 and a

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(40) Christe, K. O.; Naumann, D. *Spectrochim. Acta, Part A* **1973**, *29A*, 2017.

Table IV. Mass Spectrum of CF_3N_3

m/e	rel intens	assignt	*m/e*	rel intens	assignt
28	90	N_2	64	52	CF_2N
31	68	CF	69	100	CF_3
42	27	N_3	92	31	CF_2N_3
45	37	CFN	111	79	CF_3N_3
50	39	CF_2			

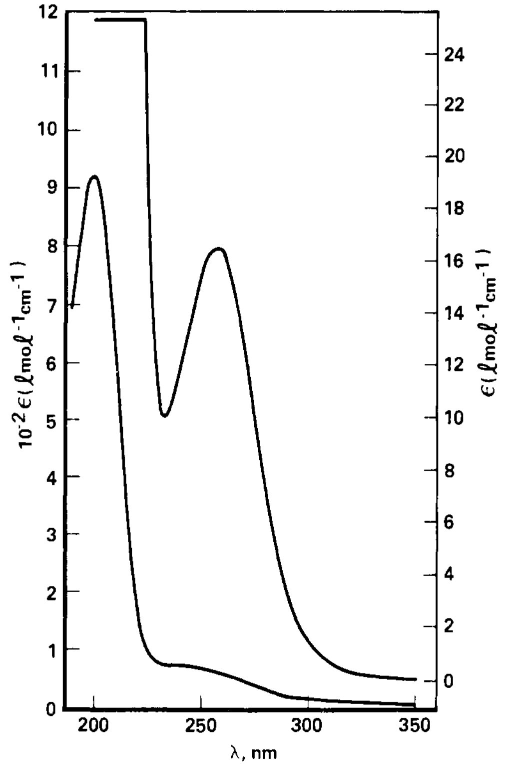
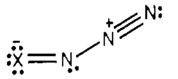


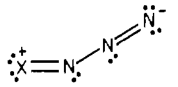
Figure 2. UV absorption spectrum of gaseous CF_3N_3.

strong N_3^+ fragment, typical for covalent azides. As expected, the base peak is due to CF_3^+, but surprisingly, the CF_3N^+ peak at *m/e* 83 was extremely weak (less than 1%), in contrast to organic azides which generally show RN^+ as base peak. However, the high intensity of the N_2^+ and CF_2N^+ peaks indicate that in CF_3N_3 N_2 elimination is also important, but that CF_3N readily loses a fluorine to form the relatively stable CF_2N radical.[41]

UV Spectrum. The UV absorption spectrum of gaseous CF_3N_3 is shown in Figure 2. The spectrum shows two strong absorptions at 200 and 258 nm, which by analogy to previous assignments for similar covalent azides[42] might be assigned to the $sp_x \rightarrow \pi y^*$ and $\pi y \rightarrow \pi x^*$ transitions of the azido group, respectively. The previous suggestions,[42] that the energy difference between these two electronic transitions in a given XN_3 molecule is both a measure for the polarity of the X–N bond and an indication for a negatively polarized chlorine in ClN_3, appear questionable. If these suggestions were correct, the replacement of the three hydrogens in CH_3N_3 by three fluorines should result in a closer match of the electronegativities of the methyl and the azido group and hence an increased covalency and a larger energy difference between the two electronic transitions. However, this is clearly not the case. The previously postulated $Cl^-{-}N_3^+$ polarization is also incompatible with the well-established[4] reaction chemistry of ClN_3 which clearly demonstrates the electropositive character of chlorine in this compound. The principle argument previously presented[4] for the $Cl^-{-}N_3^+$ polarization in ClN_3 was the relatively high frequency of the N–Hal stretching modes in ClN_3 and BrN_3. It was suggested that these high frequencies are due to partial N=X double bonding and that this partial double-bond character can only be explained by the following resonance structure invoking a formal negative charge on the halogen atom



Obviously, the possibility of the more likely resonance structure



which results also in an X=N double bond but with a positively polarized halogen was overlooked.

Summary. Azidotrifluoromethane is a relatively stable compound, and some of its physical properties were determined. The spectroscopic data show that CF_3N_3 contains a covalent azido group, similar to those of other covalent azides of known structure, such as CH_3N_3 or ClN_3. Whether the azido group is linear, as in CH_3N_3 or HN_3, or slightly bent, as in ClN_3, is difficult to say on the basis of the available data.

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Registry No. CF_3N_3, 3802-95-7.

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[41] Ogden, P. A.; Mitsch, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 3868.

[42] Dehnicke, K.; Ruschke, P. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 750.