for N_2F_4. Since all four methyl torsions appear to fall at about the same frequency, it is possible to calculate an "average" barrier assuming negligible top-top coupling. On the basis of the Mathieu equation, a periodic methyl torsional barrier of 3.4 kcal/mol is calculated from the 238-cm^{-1} band. This value is in excellent agreement with the 3.3-kcal/mol barrier obtained for the methyl torsional barrier in 1,2-dimethylhydrazine[15] but considerably lower than the 4.69-kcal/mol value for 1,1-dimethylhydrazine[16] although the latter value was for the solid state. In general, the barrier increases significantly with the addition of more methyl groups on the same nitrogen (see Table II). This trend does not appear to hold for this tetramethyl-substituted hydrazine. A possible explanation for this seemingly low barrier might be given in terms of the CNN angle which is expected to be significantly larger for this substituted hydrazine compared to the similar angle in the disubstituted hydrazines because of steric factors.

Table II. Some Barriers to Internal Rotation about C-N Bonds

Molecule	Barrier, kcal/mol	Ref	Molecule	Barrier, kcal/mol	Ref
CH_3NH_2	1.98	*a*	$(CH_3)_2NNH_2$	4.69 (solid)	*e*
$(CH_3)_2NH$	3.28	*b*	$(CH_3)_3N$	4.41	*f*
CH_3NHNH_2	3.67	*c*	$(CH_3)_2NN(CH_3)_2$	3.3	*g*
$CH_3NHNHCH_3$	3.34	*d*			

[a] D. R. Lide, Jr., and D. L. Mann, *J. Chem. Phys.*, **27**, 343 (1957). [b] K. D. Moller, A. R. DeMeo, D. R. Smith, and L. H. London, *J. Chem. Phys.*, 47, 2609 (1967). [c] J. R. Durig, W. C. Harris, and D. W. Wertz, *J. Chem. Phys.*, **50**, 1449 (1969); R. P. Lattimer and M. D. Harmony, *J. Amer. Chem. Soc.*, 73, 1400 (1971). [d] Reference 15. [e] Reference 16. [f] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **28**, 1107 (1957). [g] This work.

Although several substituted diphosphine compounds have been found to crystallize with the molecules in the trans configuration,[5,17,18] a similar result does not occur for the hydrazines. For example, tetramethyldiphosphine is approximately 60% gauche isomer at room temperature, but in the crystal the molecule has the trans structure.[17] From the one to one correspondence between the infrared and Raman frequencies in the solid state, it is quite clear that this hydrazine molecule retains the C_2 configuration in the solid. The relative energies for the trans and gauche isomers of substituted hydrazines appear to be considerably larger than the corresponding quantities for the diphosphines, since only tetrafluorohydrazine has been found to have an appreciable concentration of the trans isomer at room temperature.

Registry No. $(CH_3)_2NN(CH_3)_2$, 6415-12-9.

Acknowledgment. R. W. M. and J. R. D. acknowledge the financial support of this work by the National Aeronautics and Space Administration by Grant NGR-41-002-003. W. C. H. acknowledges support provided this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(15) J. R. Durig and W. C. Harris, *J. Chem. Phys.*, **55**, 1735 (1971).

(16) J. R. Durig and W. C. Harris, *J. Chem. Phys.*, **51**, 4456 (1969).

(17) J. R. Durig and J. S. DiYorio, *Inorg. Chem.*, **8**, 2796 (1969).

(18) Y. C. Yeung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

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Vibrational Spectrum of Bis(trifluoromethyl) Trioxide

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Received September 11, 1972

The infrared spectrum of solid $(CF_3)_2O_3$ and the Raman spectrum of gas, liquid, and solid $(CF_3)_2O_3$ have been measured in the fundamental region. A new vibrational assignment is proposed in which the symmetric O-O stretch of the triatomic O_3 bridge is located at 875 cm^{-1}, considerably higher than previously reported. This value is very similar to the value of 890 cm^{-1} for the O-O stretch in CF_3OOCF_3 and indicates a similarity in the O-O bond order in the two molecules. The high intensity of the 875-cm^{-1} band demonstrates the usefulness of Raman spectroscopy in the detection of O-O stretching vibrations.

Introduction

The infrared spectrum of gaseous CF_3OOOCF_3 has recently been reported.[1] The spectrum was assigned on the assumption that the molecule possessed only trivial C_1 symmetry. In view of the surprising stability of this substance, the vibrational frequencies of the trioxide skeleton are of particular interest. The symmetric and antisymmetric O-O-O stretching frequencies were assigned[1] to strong infrared bands at 773 and 897 cm^{-1}, respectively.

More recently, the structures of $(CF_3)_2O$, $(CF_3)_2O_2$, and $(CF_3)_2O_3$ were investigated by electron diffraction.[2] An O-O bond length of about 1.5 Å and an O-O-O of 120° was found for the trioxide. This bond length corresponds to an O-O single bond as found, for example, in hydrogen peroxide, HOOH. Durig and Wertz[3] have examined the infrared and Raman spectra of CF_3OOCF_3. They assigned the strongest Raman band in the spectrum at 886 cm^{-1} to the O-O stretching vibration. Because of the large polarizability change associated with symmetric motions of this type, Raman spectroscopy is particularly well

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(1) R. P. Hirschmann, W. B. Fox, and L. R. Anderson, *Spectrochim. Acta, Part A*, **25**, 811 (1969).

(2) S. H. Bauer, Abstracts, 3rd Austin Symposium on Gas Phase Molecular Structure, March 1970.

(3) J. R. Durig and D. W. Wertz, *J. Mol. Spectrosc.*, **25**, 467 (1968).

suited for studying substances containing the O-O linkage. Therefore, we felt that it would be of considerable interest to examine the Raman spectrum of CF_3OOOCF_3 in order to establish better the vibrational assignment for the skeletal stretching and bending motions. The results of this investigation along with some partially completed results on $(CF_3)_2O$ are presented in this paper.

Experimental Section

The sample of $(CF_3)_2O_3$ used in this study was prepared by a modification of a method described in literature.[4] Excess oxygen difluoride and cesium trifluoromethoxide[5] were allowed to react in a 75-ml stainless steel vessel at 40° for 2 days. The $(CF_3)_2O_3$ formed was purified by collecting it in a −125° trap while pumping on the reactor as it warmed slowly from −196°.

The sample of $(CF_3)_2O$ used in this study was supplied by Dr. L. R. Anderson of Allied Chemical Corp. This sample contained considerable amounts of COF_2 which was removed by condensation of the sample on wet KOH.

The infrared spectrum of solid $(CF_3)_2O_3$ was measured at liquid nitrogen temperature on a Perkin-Elmer Model 621 spectrophotometer using a cold cell of conventional design. The Raman spectrum of liquid $(CF_3)_2O_3$ sealed in a capillary tube was recorded with a Cary Model 82 Raman spectrometer.[6] The spectrum of the gas was obtained with the sample contained in a standard Cary multipass gas cell. Low-temperature studies were carried out using a cold cell similar to the one described by Harney and Miller.[7]

Results and Discussion

In the previously published analysis of the vibrational spectrum of $(CF_3)_2O_3$, only trivial C_1 symmetry was assumed. However, the electron diffraction data can be interpreted in terms of C_2 symmetry. Moreover, our study reveals a number of depolarized Raman lines which is not consistent with C_1 symmetry. Even though one sometimes observes measured ratios for symmetric modes which are indistinguishable from the theoretical value expected for a depolarized band, the fact that nearly half of the observed Raman lines are depolarized favors the presence of a symmetry element. Therefore, we have chosen to interpret our data in terms of C_2 symmetry. The molecular vibrations are thus described in terms of in-phase and out-of-phase motions of two CF_3O groups. This approach has the advantage of allowing one to associate strong, polarized Raman bands with in-phase motions, whereas strong infrared bands are associated with the out-of-phase motions. (See Table I.)

A survey scan of the mid-infrared spectrum of gaseous CF_3OOOCF_3 was identical with that published by Hirschmann, *et al.*[1] Therefore, in our discussion of the vibrational assignments we shall use the infrared frequencies previously reported. The six C-F stretching motions have been assigned[1] to infrared bands at 1290, 1252, and 1169 cm^{-1}. In the Raman spectrum of the solid shown in Figure 1B, six bands were observed which are assignable as C-F stretching modes.

There are two motions involving symmetric and antisymmetric C-O stretches. The symmetric C-O stretch should be intense in the Raman spectrum, and we find a polarized band of medium intensity at 930 cm^{-1} which has a medium-intensity infrared counterpart. The antisymmetric C-O stretch is expected to be intense in the infrared spectrum and would normally occur at a higher frequency than the corresponding symmetric mode. Hirschmann, *et al.*,[1] assigned a medium-intensity infrared band at 997 cm^{-1} as the antisymmetric C-O stretch. However, the only strong infrared band in the region occurs at 897 cm^{-1}, and we assign the band as the antisymmetric stretch. This is a rather low frequency since this motion occurs at 1065 cm^{-1} in CF_3OOCF_3.[3] In discussing the antisymmetric C-O stretch it is also useful to consider the molecule bis(trifluoromethyl) ether, $(CF_3)_2O$. A mid-infrared spectrum of this substance is shown in Figure 2 and Table II. The type "A" band centered at 970 cm^{-1} can be confidently assigned as the antisymmetric C-O stretch on the basis of its relative intensity, band contour, and measured P-R separation.[8] Due to a limited amount of sample, it was not possible to obtain the Raman spectrum of this substance. Therefore, assignment of the symmetric C-O stretch in $(CF_3)_2O$ is still uncertain. A comparison of the C-O bond lengths and C-O stretching assignments for $(CF_3)_2O_n$ ($n = 1, 2, 3$) is presented in Table III. There seems to be some correlation between the increasing C-O bond length and decreasing C-O stretching frequency, although $\nu_{antisym}$ is out of line for CF_3OOCF_3. A possible difficulty in attempting to make such a comparison is that in $(CF_3)_2O$, a COC angle bend may be involved with a C-O stretch, whereas the C-O stretch may interact with a COO angle bend in the peroxide and trioxide.

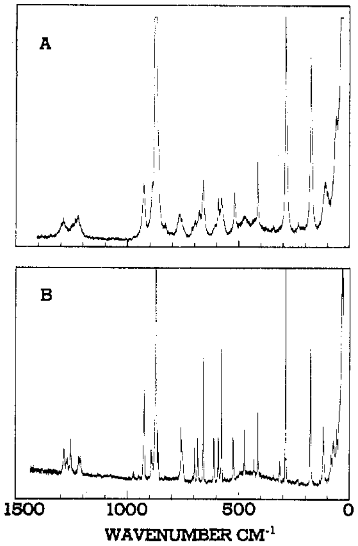

Figure 1. Raman spectra of CF_3OOOCF_3 with 5145-Å excitation: A, spectrum of liquid at room temperature; B, spectrum of solid at −150°.

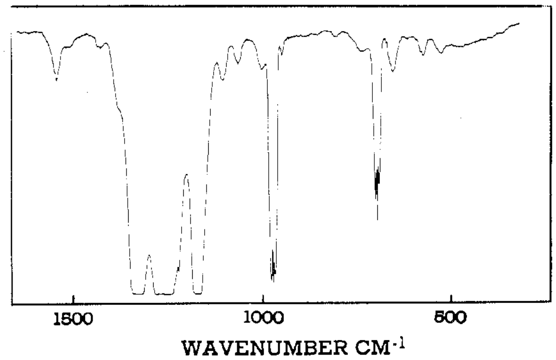

Figure 2. Mid-infrared spectrum of gaseous $(CF_3)_2O$.

The most interesting aspect of the vibrational assignment

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(4) L. R. Anderson and W. B. Fox, *J. Amer. Chem. Soc.*, 89, 4313 (1967).

(5) D. D. DesMarteau, *Inorg. Chem.*, 9, 2179 (1970).

(6) The Raman spectrophotometer was purchased with funds from National Science Foundation Grant GP-28068.

(7) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, 24, 291 (1970).

(8) The following parameters were assumed for $(CF_3)_2O$: C-F = 1.32 Å, C-O = 1.36 Å, C-O-C = 124°, and tetrahedral angles in the CF_3 groups. These parameters lead to a calculated P-R separation of 10.6 cm^{-1} for a type A band.

Table I. Infrared and Raman Frequencies (cm^{-1}) of Bis(trifluoromethyl) Trioxide[a]

Infrared				Raman						
Gas	Rel intens	Solid	Rel intens	Gas	Liquid	Rel intens	Polarizn	Solid	Rel intens	Assignment
								1285	w	
1290	vs			1293		w		1275	w	
					~1285 b			1270	w	
1252	vs			1250		w?		1255	w	ν_1–ν_3, ν_{15}–ν_{17}, C–F str
								1221	w	
		1200	b	1230	~1220 b	w?		1214	w	
								1210	w	
1185	sh									
1169	vs									
1067	m									$\nu_{18} + \nu_{12} = 1071$
997	m									
								973	vw	
								950	vw	
929	m	924		930	927	m	p	926	s	ν_4, sym C–O str
897	s	894	m					894	w	ν_{18}, antisym C–O str
		888	sh					887		
				875	873	vs	p	873	vvs	ν_5, sym O_3 str
								863	w	
1810?	w?									
		779	w							
773	s	761		771	765 b?	m	dp	759	m, b	ν_{19}, antisym O_3 str
755	sh	750	w					752		
699	m	698	m	~696	698	w	dp	699	m	ν_{20}, sym CF_3 def
		684	w	679	680	w	dp	685	m	
660	m	656	m	661	660	m	p	659	s	ν_6, sym CF_3 def
630	m?									
		613	w		610	m	dp	612	m	ν_{21}, antisym CF_3 def
		593	w	593	593	m	p	592	m	ν_7, antisym CF_3 def
577	s	579	m	577	578	m	dp	578	s	ν_{22}, antisym CF_3 def
525	vw	523	m	521	523	m	p	525	m	ν_8, antisym CF_3 def
474	m	475	m		473	w, b	dp	475	m	ν_{23}, CF_3 rock
		433	vw					432	vw	
		417	vw	415	414	m	p	415	m	ν_9, ν_{10}, CF_3 rock
318	m	317	m					318	vw	ν_{24}, CF_3 rock
286	w			286	288	vs	p	288	vs	ν_{11}, O_3 skeletal bend
174	w			173	175	s	p	177	s	ν_{12}, C–O–O skeletal bend
124	w			115	115	m	dp	120		ν_{25}, C–O–O skeletal bend
								84	w	
								73	w	ν_{13}, ν_{14}, ν_{26}, ν_{27} CF_3 and skeletal torsions
					~68 b	w		59	w	
								~45	w	
								37	w	
								33	w	
								27	w	

[a] Abbreviations used: s, strong; m, medium; v, very; w, weak; sh, shoulder; b, broad; p, polarized; dp, depolarized. [b] The vibrational assignment is made under C_2 symmetry. ν_1–ν_{14} are in-phase A species vibrations, whereas ν_{15}–ν_{27} are out-of-phase B species motions.

Table II. Mid-Infrared Spectrum of Bis(trifluoromethyl) Ether with Suggested Vibrational Assignments[a]

Freq, cm^{-1}	Rel intens	Assignment
1328	vvs	CF_3 str
1255	vvs	CF_3 str
1178	vvs	CF_3 str
1173		
1102	w	576 + 527 = 1107
1061	w	527 × 2 = 1054
999	w	
975.0 R		
970.0 Q	s, type A	Antisym C–O str
964.4 P		
946	w	
700.0 R		
695.0 Q	m, type A	Out-of-phase sym CF_3 def
689.4 P		
579	w	Antisym CF_3 def
573		
527	w	Antisym CF_3 def

[a] Abbreviations used: vvs, very, very strong; w, weak; s, strong; m, medium; R, Q, P, rotational structure of gas-phase band.

Table III. A Comparison of the C–O Bond Distance and the C–O Stretching Assignments for Three CF_3O-Containing Molecules

	ν_{asym}, cm^{-1}	ν_{sym}, cm^{-1}	r_{C-O}, Å[a]
$(CF_3)_2O$	970		1.360
$(CF_3)_2O_2$	1065	975	1.398
$(CF_3)_2O_3$	897	929	1.407

[a] Distance taken from ref 2.

for $(CF_3)_2O_3$ is the group of frequencies associated with the trioxide bridge. Hirschmann, *et al.*,[1] assigned the antisymmetric and symmetric O-O-O stretching frequencies to strong infrared bands at 897 and 773 cm^{-1}, respectively. In the Raman spectrum, these bands appear only weakly, whereas we find a very strong polarized band at 875 cm^{-1}. This latter band does not appear in the infrared spectrum. On the basis of its strong Raman intensity, the 875-cm^{-1} band is assigned as the symmetric O-O-O stretch. The high intensity of this band indicates the usefulness of Raman spectroscopy in detecting the O-O linkage in such molecules. Melveger, *et al.*,[9] have reached a similar con-

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(9) A. J. Melveger, L. R. Anderson, C. T. Ratcliffe, and W. B. Fox, *Appl. Spectrosc.*, 26, 381 (1972).

Table IV. Comparison of HF pure Rotational Spectrum with Absorptions in the Far-Infrared Spectrum of CF_3OOOCF_3

Transition $J' \leftarrow J$	Obsd freq for HF,[12] cm^{-1}	Obsd freq of Hirschmann, *et al.*,[1] cm^{-1}	Transition $J' \leftarrow J$	Obsd freq for HF,[12] cm^{-1}	Obsd freq of Hirschmann, *et al.*,[1] cm^{-1}
$2 \leftarrow 1$	82.35	83	$5 \leftarrow 4$	204.50	205
$3 \leftarrow 2$	122.83	124	$6 \leftarrow 5$	244.97	245
$4 \leftarrow 3$	163.92	164	$7 \leftarrow 6$	284.98	285

clusion in their Raman study of a series of peroxides. Our study also indicates the usefulness of obtaining both the infrared and Raman spectra of these type of molecules in arriving at the correct vibrational assignment, particularly for the symmetric vibrations.

Having given a reasonable assignment for the symmetric skeletal stretch, it is necessary to consider the antisymmetric skeletal stretch. This band should be strong in the infrared region, and the strongest infrared band in the spectrum (with the exception of the CF_3 stretches) occurs at 773 cm^{-1}. This band is broad and depolarized in the Raman spectrum as would be expected for an antisymmetric stretch. Moreover, it is too high in frequency to be a symmetric CF_3 deformation. Therefore, the 773-cm^{-1} band is assigned as the antisymmetric O-O-O stretch. A possible objection to this assignment is the fact that the symmetric stretch occurs at a higher frequency than the antisymmetric stretch. However, there is precedent for this reversal in the vibrational spectrum of the simplest trioxide, ozone. In ozone,[10] the symmetric O-O stretch occurs at 1110 cm^{-1} whereas the antisymmetric stretch appears at 1043 cm^{-1}. Therefore, it does not seem unreasonable that a similar situation might occur in the $(CF_3)_2O_3$ molecule. It should be noted, however, that bond lengths in O_3 and $(CF_3)_2O_3$ are quite different, 1.28 and 1.51 Å, respectively.[11] The value of 1.51 Å is approximately that of an O-O single bond (as in HOOH), while the 1.28-Å value in O_3 is indicative of some double-bond character.

The vibrations between 700 and 300 cm^{-1} can be assigned to deformations and rocking motions of the CF_3 groups. The medium-intensity infrared bond at 699 cm^{-1} with a weak depolarized Raman counterpart is assigned as the out-of-phase symmetric CF_3 deformations. In CF_3OOCF_3, the out-of-phase symmetric deformation occurs at 673 cm^{-1}, whereas, in CF_3OCF_3, this motion occurs at 695 cm^{-1}. The in-phase component is assigned to a polarized Raman band at 660 cm^{-1}. The two in-phase antisymmetric CF_3 deformations are assigned to bands at 593 and 521 cm^{-1}, whereas the out-of-phase components appear at 610 and 577 cm^{-1}. There are also four CF_3 rocking vibrations. The two in-phase components, ν_9 and ν_{10}, are assigned to a polarized Raman band at 415 cm^{-1}. The out-of-phase components, ν_{23} and ν_{24}, are assigned to medium-intensity infrared bands at 474 and 318 cm^{-1}. These assignments of the CF_3 deformations and rocks are in general agreement with those of Hirschmann, *et al.*,[1] so that no detailed comparison of the assignment is necessary.

The second strongest Raman band appears at 286 cm^{-1}. This polarized band is obviously a symmetric motion, and on the basis of its intensity, we assign it as the skeletal bending motion of the O_3 bridge. The in-phase and out-of-phase F_3C-O-O bending motions are assigned to bands at 174 and 124 cm^{-1}, respectively, in agreement with Hirschmann, *et al.*[1] The higher frequency band is intense and polarized as one would expect for a symmetric motion, while the lower frequency band is broad and depolarized.

In the Raman spectrum of the liquid, we observe a broad band of uncertain polarization centered near 60 cm^{-1}. Upon solidification, we observe bands at 84, 73, 59, 45, 37, 33, and 27 cm^{-1}. Some of the bands may be due to CF_3 torsional motions. It is difficult to make any specific assignment; however, lattice vibrations could account for many of the bands, especially those below 50 cm^{-1}.

A final point of interest is the set of five lines observed by Hirschmann, *et al.*,[1] in the far-infrared spectrum of gaseous $(CF_3)_2O_3$. These lines were stated to occur with a regular spacing of 40 cm^{-1} and were found to be extremely sharp. The authors state that no ready explanation for these lines was apparent. However, an examination of Table IV reveals excellent agreement between the lines previously reported in $(CF_3)_2O_3$ and the pure rotational spectrum of HF.[12] The $J = 2 \rightarrow 3$ transition of HF at 122.83 cm^{-1} is obscured by a fundamental mode of $(CF_3)_2O_3$ at 124 cm^{-1}. The HF rotational spectrum has caused considerable difficulty in assigning the far-infrared spectrum of many fluorine-containing molecules.[13]

Registry No. $(CF_3)_2O_3$, 1718-18-9; $(CF_3)_2O$, 1479-49-8.

Acknowledgment. The authors (J. D. W. and J. R. D.) gratefully acknowledge the financial support given this work by the National Aeronautics and Space Administration by Grant NGL-41-002-003. We also wish to thank Dr. L. R. Anderson for providing the sample of $(CF_3)_2O$ used in this study.

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(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 83.

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 410.

(12) W. G. Rothschild, *J. Opt. Soc. Amer.*, 54, 20 (1964).

(13) See, for example, the case of PF_5: L. C. Hoskins, *J. Chem. Phys.*, 42, 2631 (1964), and references therein.