Inorg. Chem. **1980**, *19*, 1699–1701

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Microwave Spectrum and Structure of CF_3OOF

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Received December 31, 1979

The microwave spectrum of (fluoroperoxy)trifluoromethane has been recorded from 18.5 to 40.0 GHz. Only a-type transitions were observed. The R-branch assignments have been made for the ground state and two vibrational excited states. The three rotational constants for the ground vibrational state are $A = 4918.2 \pm 11.3$, $B = 1942.22 \pm 0.05$, and $C = 1870.19 \pm 0.05$ MHz. From a diagnostic least-squares adjustment to fit the three rotational constants the following structural parameters were obtained: $\angle FOOC = 96.3 \pm 7.6°$, $\angle OOF = 103.7 \pm 6.2°$, $r(O–O) = 1.380 \pm 0.026$ Å, $r(O–F) = 1.434 \pm 0.018$ Å, $r(C–O) = 1.404 \pm 0.019$ Å, and $\angle tilt = 5.0 \pm 0.7°$ with reasonable assumptions for the three other structural parameters. These parameters are compared to the corresponding ones in some other peroxides. From the relative intensity of the ground and the excited vibrational state, the CF_3 torsion is calculated to have a frequency of 70 ± 5 cm^{-1}. From this frequency the threefold barrier to internal rotation was calculated to have a value of 2.8 ± 0.4 kcal/mol. The relatively large uncertainty in the barrier value results from the frequency uncertainty coupled with the very small F number. This CF_3 barrier is compared to the corresponding quantity in similar molecules.

Introduction

The highly fluorinated peroxides have rather large variations in their structural parameters. For example the O–O bond distance in O_2F_2 has been reported[1] to be 1.219 Å which is near the double-bond distance in the O_2 molecule.[2] However the O–O distance in the CF_3OOCF_3 has been reported[3] to be 1.419 Å which is close to the O–O bond length (1.46 Å) in the H_2O_2 molecule.[4,5] Similarly, the O–F bond distance (1.579 Å) in O_2F_2 is quite long compared to the corresponding distance of 1.409 Å in the OF_2 molecule.[6] Thus, the structural parameters of the (fluoroperoxy)trifluoromethane, CF_3OOF, molecule are of considerable interest in establishing trends in the structural parameters of these peroxides and in the theoretical prediction of molecular structures related to O_2F_2.[7]

Recently a gas-phase electron diffraction study[8] was reported for CF_3OOF and the ten geometrical parameters were extracted from five distinct and two poorly defined peaks. From these data, two least-squares minima were found. The first one, which was preferred by the investigators[8] since all parameters converge successfully, had an $r(O–F)$ distance of 1.449 ± 0.015 Å and an $r(O–O)$ distance of 1.366 ± 0.033 Å whereas the second one had an $r(O–F)$ distance of 1.385 ± 0.015 and an $r(O–O)$ distance of 1.454 ± 0.018 Å. The other structural parameters were about the same except for the tilt of the CF_3 moiety which was found to be $3.9 \pm 1.8°$ for the first minimum and $6.7 \pm 1.2°$ for the second minimum. It should be mentioned that the second minimum could only be made to converge if one parameter such as the O–F bond length or the O–O–F bond angle was fixed. Thus, the electron diffraction investigators[8] concluded that minimum two was an artifact which resulted from the limited resolution of the overlapping distances obtainable by their study. In addition to the unstable behavior in the least-squares refinements and the poorer fit with minimum two, it was also noted that the values of several of the structural parameters for this fit did not agree as well as those found[7] for the CF_3OOH and CF_3OOCl molecules. Therefore, for additional information on the structural parameters of CF_3OOF, a microwave study of this molecule was undertaken. In addition it was hoped to obtain information on the barrier to internal rotation of the CF_3 moiety. The results of this microwave study are reported herein.

Experimental Section

The sample of (fluoroperoxy)trifluoromethane was prepared and purified by standard procedures.[9] The microwave spectra were obtained by using a Hewlett-Packard 8460A MRR spectrometer with a Stark modulation frequency of 33.3 kHz. The Stark cells were maintained at dry ice temperature for all measurements except those of relative intensity, which were performed at room temperature (~24 °C). The sample was continually flowed through the waveguide to minimize decomposition effects. Also the waveguide was baked overnight at 70 °C with continual vacuum pumping. With these procedures decomposition was not a problem at −40 °C.

Microwave Spectrum and Results

If the atoms COOF were coplanar in CF_3OOF, the molecule would have a symmetry plane and one would expect only two types of rotational transitions. On the basis of the structure obtained from the gas-phase electron diffraction investigation,[8] CF_3OOF does not have any symmetry element except C_1. Thus, one may expect a-, b-, and c-type transitions for this molecule. With the ED structural parameters, a calculation of the moments of inertia has indicated that CF_3OOF is a nearly prolate rotor with a κ value around −0.95.

As shown in Figure 1, the microwave spectrum of CF_3OOF is typically that of a nearly symmetric rotor. The four nearly equal-spaced bands in the R-band frequency region may, thus, be assigned as the $6 \rightarrow 7$, $7 \rightarrow 8$, $8 \rightarrow 9$, and $9 \rightarrow 10$ a-type transitions, respectively. Each individual line has a half-width of 0.2 MHz under our experimental conditions. Thus, under favorable conditions, the accuracy of the frequency measurements is expected to be better than 0.05 MHz. Initial assignments of the low-K transitions were based essentially on the qualitative Stark information. In addition to these four major bands there are two series of progressions of lines originating near the 29.5-GHz frequency region which appeared if the flow rate was not sufficiently high. One series has successive lines decreasing in frequency while the other series has increasing frequency for successive lines. Both series of lines are believed to be caused by an impurity formed by the decomposition of the sample in the waveguide, since their relative intensities to the major bands depended on the ex-

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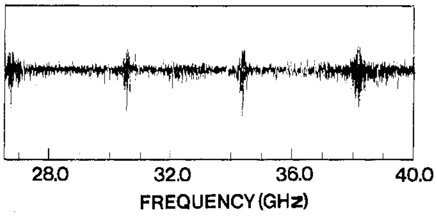

Figure 1. Low-resolution microwave spectrum of CF_3OOF in the region 26.5–40.0 GHz. The base-peak Stark voltage is 1000 V.

Table I. Ground-State Rotational Transitions (MHz) of CF_3OOF

transitn	ν(obsd)	ν(obsd) – ν(calcd)[a]
$5_{05}-4_{04}$	19 036.60	0.26
$5_{15}-4_{14}$	18 876.70	0.24
$5_{14}-4_{13}$	19 236.57	0.23
$5_{24}-4_{23}$	19 059.35	0.16
$5_{23}-4_{22}$	19 085.06	0.16
$6_{06}-5_{05}$	22 829.88	0.18
$6_{16}-5_{15}$	22 648.59	0.17
$6_{15}-5_{14}$	23 079.97	0.14
$6_{25}-5_{24}$	22 868.73	0.08
$6_{24}-5_{23}$	22 913.53	0.11
$7_{07}-6_{06}$	26 615.90	0.05
$7_{17}-6_{16}$	26 418.73	0.04
$7_{16}-6_{15}$	26 921.19	0.07
$7_{26}-6_{25}$	26 676.90	0.06
$7_{25}-6_{24}$	26 747.79	−0.06
$8_{08}-7_{07}$	30 393.95	−0.14
$8_{26}-7_{25}$	30 588.53	−0.14
$9_{09}-8_{08}$	34 163.57	−0.49
$9_{27}-8_{26}$	34 435.61	−0.41

[a] Calculated from the rotational constants given in Table II.

Table II. Rotational Constants (MHz) and Moments of Inertia[a] (U Å^2) of CF_3OOF in the Ground Vibrational State

A	4918.2 ± 11.3	I_a	102.76
B	1942.22 ± 0.05	I_b	260.213
C	1870.19 ± 0.05	I_c	270.235
κ	−0.9527		

[a] Conversion factor: 505 391 MHz = 1 U Å^2.

Table III. Rotational Transitions and Rotational Constants (MHz) of CF_3OOF in Excited Vibrational States

	$\nu = 1$		$\nu = 2$	
transitn	ν(obsd)	$\Delta\nu$(obsd – calcd)[a]	ν(obsd)	$\Delta\nu$(obsd – calcd)[a]
$9_{19}-8_{18}$	33 982.60	0.22	34 006.69	0.28
$9_{18}-8_{17}$	34 612.06	0.23	34 625.67	0.27
$10_{010}-9_{09}$	37 956.02	−0.12	37 981.19	−0.02
$10_{110}-9_{19}$	37 750.05	−0.09	37 776.99	−0.06
$10_{19}-9_{18}$	38 445.66	−0.10	38 461.14	−0.06
$10_{28}-9_{27}$	38 308.14	−0.10	38 136.84	−0.35
	$A = 4906.2 \pm 17.3$		$A = 4895.3 \pm 25.0$	
	$B = 1942.72 \pm 0.04$		$B = 1943.11 \pm 0.06$	
	$C = 1872.08 \pm 0.04$		$C = 1873.66 \pm 0.06$	
	$\kappa = -0.953\,42$		$\kappa = -0.954\,02$	

[a] ν(calcd) is calculated from the rotational constants given below the transitions.

Table IV. Structural Parameters[a] and Calculated Rotational Constants (MHz) of CF_3OOF

	ED (I)	ED (II)	MW (I)	MW (II)
r(C-F)	1.322	1.318	1.322[b]	1.318[b]
r(C-O)	1.419	1.415	1.419[b]	1.415[b]
∠COO	108.2	105.7	108.2[b]	105.7[b]
∠FCF	109.0	110.6	109.0[b]	110.6[b]
∠FOO	104.5	105.0	104.5[b]	105.0[b]
r(O-O)	1.366	1.454	1.373	1.398
r(F-O)	1.449	1.385	1.418	1.454
∠FOOC	97.1	99.9	93.9	94.5
∠tilt	3.9	6.7	4.83	5.05
A	4941.75	4927.28	4918.12	4924.83
B	1914.19	1902.72	1942.23	1941.30
C	1841.66	1847.53	1870.19	1871.02

[a] All bond distances are in units of angstroms and angles in degrees. [b] Assumed value.

perimental conditions such as sample flow rate and temperature.

In Table I are listed the observed frequencies for a number of low-K R-branch transitions of μ_a type in the ground vibrational state of CF_3OOF. A search for b- and c-type transitions turned out to be unsuccessful, probably due to the small dipole moments along the b- and c-axis directions. Since CF_3OOF is nearly a prolate rotor, the parallel transitions are relatively insensitive to the magnitude of the rotational constant, A. In order to obtain a better rotational constant A, we measured two more series of higher J transitions, $(J + 1)_{0,J+1} \leftarrow J_{0,J}$ and $(J + 1)_{2,J-1} \leftarrow J_{2,J-2}$, which are more sensitive to the A moment than the other a-type R-branch transitions involving the same J levels. As can be seen from Table I, the deviations of the calculated from the observed frequencies vary regularly with both K_{-1} and J values in the transitions. This suggests a contribution from the centrifugal distortion effect. No attempt has been made to determine the centrifugal distortion constants because the measured transitions involved only a small range of rotational quantum numbers. With use of the rigid rotor model, a least-squares fit to the measured frequencies as listed in Table I gave the rotational constants listed in Table II. The uncertainty of the rotational constants given in this table represents 3 times the standard dispersion.

In addition to the ground-state line for each rotational transition, there are other weaker satellite lines. These lines arise from the molecules in several of the excited vibrational states. The most intense satellites were measured and are listed in Table III under the column $v = 1$. Since the CF_3 torsion is expected to have the lowest vibrational frequency, the most intense satellite is assigned to the molecule in the first excited CF_3 torsional state. Relative intensity and position suggest that the second satellite which we measured (see Table III) is due to the molecule in the second CF_3 excited torsional state. No splittings due to the internal rotation motions were observed in either the ground or the excited states which we measured in the present investigation. Relative intensity measurements gave a frequency of 70 ± 5 cm^{-1} for the first CF_3 torsional mode. The uncertainty arises essentially from the possible interference of some other unidentified satellite lines.

Discussion

Because of the numbers of parameters involved in the structure of CF_3OOF, it is impossible to obtain a complete structure from the results of the present microwave study. Marsden, DesMarteau, and Bartell[8] have investigated the molecular structure of CF_3OOF by using the gas-phase electron diffraction method. Their results are reproduced in Table IV under columns ED (I) and ED (II). Both sets of parameters represent two different least-squares minima. Due to its better fit, the stable behavior in the least-squares refinements, and the similarity of some of the parameters with those of other similar molecules, the structure under column ED (I) was considered to be the preferred one. With these ED structures, we have carried out a least-squares fit to the experimental rotational constants, and the results are also listed in Table IV. The structure listed under column MW (I) was obtained in reference to the ED (I) parameters while those under column MW (II) are based on the ED (II). MW (I) parameters reproduce the experimental rotational constants much better than MW (II) and should be considered as the more favorable structure than the MW (II) parameters. This

Table V. Diagnostic Least-Squares Adjustment of the Structural Parameters in CF_3OOF

parameter	starting value	estd uncertainty	adjusted value	ED (I)
r(C-F), Å	1.322	fixed		1.322 ± 0.009
r(C-O), Å	1.42	±0.03	1.404 ± 0.019	1.419 ± 0.024
∠COO, deg	108.0	fixed		108.2 ± 1.2
∠FCF, deg	109.5	fixed		109.0 ± 1.0
∠FOO, deg	105	±10	103.7 ± 6.2	104.5 ± 4.5
r(O-O), Å	1.39	±0.03	1.380 ± 0.026	1.366 ± 0.033
r(F-O), Å	1.44	±0.02	1.434 ± 0.018	1.449 ± 0.015
∠FOOC, deg	96	±10	96.3 ± 7.6	97.1 ± 6.0
∠tilt, deg	5.0	±2.0	5.0 ± 0.7	3.9 ± 1.8

is reflected by the magnitude of the standard deviations [0.001 for the MW (I) and 0.220 for the MW (II)]. In both calculations, it was impossible to obtain a reasonable fit to the experimental rotational constants by assuming a zero tilt angle for the CF_3 group. The resultant tilt angles in both cases are very close to 5°, and this angle should be considered to be a significant parameter. It is of interest to note that both calculations yield a similar dihedral angle (~94°) for the COOF atoms.

In order to obtain the uncertainty in the structural parameters, we allowed them to vary by using the method of diagnostic least squares as described by Curl.[10] The initial starting values with the estimated uncertainties as well as the refined parameters are listed in Table V. The refined parameters along with their uncertainties are compared to the ED (I) parameters with their accompanying uncertainties. These refined parameters give the following calculated rotational constants: $A = 4919.3$, $B = 1942.87$, and $C = 1870.52$ MHz which agree very well with the experimental values. The O–O distance is slightly longer than the value from the ED study, and the C–O and F–O distances are slightly shorter, but if one considers the uncertainties, there is excellent agreement between the two results.

The tilt angles in CF_3OOH and CF_3OOCl were found to be 4.8° and 5.1°, respectively, and the value of 5.0° found in this microwave study of CF_3OOF appears to be consistent with the values for these other peroxides. The F–O bond distance of 1.434 Å is larger than the similar distance[6] in OF_2[r(F–O) = 1.409 Å]. The same similarity was found[7] between the Cl–O distances in CF_3OOCl and Cl_2O.

The O–O bond distance of 1.380 Å is considerably shorter than the similar distance for CF_3OOCl and CF_3OOH [r(O–O) = 1.447 Å for both molecules[7]]. For the latter two molecules, the O–O bond distance is essentially the same as that found in the H_2O_2 [r(O–O) = 1.46 Å] molecule.[4,5] The O–O bond distance[1] in the O_2F_2 is 1.219 Å which is extremely short. Thus, the shorter O–O distance in CF_3OOF compared to the other peroxides seems appropriate with the substitution of the F atom for H or Cl. This distance indicates that the CF_3OOF molecule should be more like CF_3OOH or H_2O_2 than like O_2F_2. As pointed out in the electron diffraction study,[8] there appears to be a reasonable trend for the O–O distances among the CF_3OOF (1.380 Å), CF_3OOCF_3 (1.419 Å) and CF_3OOH (1.447 Å) molecules. It should also be mentioned that the longer C–O distance (1.404 Å) in CF_3OOF compared to the similar distances in CF_3OOCl (1.372 Å) and CF_3OOH (1.376 Å) is consistent with the shortening of the O–O distance in (fluoroperoxy)trifluoromethane. All of these trends appear to support the structural parameters obtained in this microwave study of the CF_3OOF molecule and also support the structural parameters obtained from the first minimum, ED (I), in the electron diffraction study.

From the structure listed as MW (I) we calculated the F number ($F = h^2/8\pi^2 I_r$ where $I_r = I_\alpha(1 - \sum_i \lambda^2_i I_\alpha / I_i)$ where I_r is the reduced moment of inertia for the internal rotation, I_α is the moment of inertia of the internal top, I_i is the ith principal moment of inertia of the entire molecule, and λ_i is the cosine of the angle between the axis of the internal top and the ith principal axis of the molecule) to be 0.5715 cm^{-1} for the CF_3 rotor. From the torsional frequency (70 cm^{-1}) and the F number, the threefold periodic barrier (V_3) for the internal rotation was calculated to be 990 cm^{-1} (2.8 kcal/mol). Since the CF_3 rotor is such a heavy top and the uncertainty of the torsional frequency is relatively large (±5 cm^{-1}), the deviation of the calculated barrier is significant. For example, with a torsional frequency of 75 cm^{-1} the calculated barrier is 3.23 kcal/mol whereas a torsional frequency of 65 cm^{-1} gives a barrier of 2.46 kcal/mol. An investigation of the Raman spectrum of this molecule in the gas phase would probably provide a more accurate measurement (±1 cm^{-1}) of the torsional fundamental. Frequently it is found that the torsional overtone is observed in the Raman spectrum for molecules with the CF_3 moiety, but sometimes it is difficult to determine whether one is observing the fundamental or the overtone. The torsional frequency obtained in this study should place sufficient constraints on the torsional frequency so the fundamental can be confidently assigned from a vibrational study.

The barrier of 2.8 kcal/mol seems low when compared to the value of 4.8 kcal/mol obtained for the CF_3OF molecule.[11] However, the longer C–O bond distance (1.404 Å) in CF_3OOF compared to the similar distance[12] (1.395 Å) in CF_3OF suggests that the barrier may be significantly different in CF_3OOF. In view of the CF_3 barrier in CF_3OOF it appears that the corresponding barrier of 0.73 kcal/mol in CF_3OOCF_3 is probably too low.[13] However, the value of 5.4 kcal/mol reported[14] earlier from a vibrational study appears to be more consistent with the CF_3 barrier in CF_3OOF and seems to be supported by a recent electron diffraction study[15] of CF_3OOCF_3. Preliminary data indicate that the CF_3 rotor barriers might provide the theoreticians with some excellent results with which to check the sensitivity of their calculations. Also, it appears that this is an area where further studies are warranted.

Acknowledgment. The authors gratefully acknowledge the financial support of this study by the National Science Foundation by Grants CHE-76-23542 and CHE-78-04077.

Registry No. CF_3OOF, 34511-13-2.

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