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The Infrared and Raman Spectra of Bis(trifluoromethyl)peroxide

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NGR-41-002-003

Abstract----The gas phase infrared spectrum as well as the liquid phase Raman data of bis(trifluoromethyl)peroxide are reported from 33 cm^{-1} to 3000 cm^{-1} and from 200 cm^{-1} to 1400 cm^{-1}, respectively. An assignment of the twenty-four normal modes is suggested and discussed. Only one CF_3 torsion is found at 64 cm^{-1}, and the barrier to internal rotation is calculated to be 5.4 kcal/mole. The 0-0 torsional mode is also observed, but due to a lack of data only a very rough estimate may be given for the cis barrier, 16 ± 6 kcal/mole.

INTRODUCTION

Peroxides, due to their instability, form a class of molecules about which little or no spectroscopic work has been done. Only hydrogen peroxide has been extensively studied. Arvia and Aymonino[1] have studied the infrared spectra of the two peroxides $(FCO)_2O_2$ and $(CF_3)_2O_2$, but their studies were limited to the frequency range above 400 cm^{-1} so that they were unable to examine the skeletal bending modes or the torsional oscillations. Their assignments were based on a comparison of the spectra of the two molecules. Thus, to our knowledge, no study of the skeletal bending modes for a C-O-O-C skeleton has been reported and, consequently, it was believed that the investigation of the far infrared spectrum of $(CF_3)_2O_2$ would be of considerable interest. Examination of the Raman effect of the $(CF_3)_2O_2$ molecule was expected to lead to an unambiguous assignment of the skeletal stretching fundamentals and to a definite decision on the symmetry of this peroxide. However, not only are the skeletal motions of this molecule expected to be of interest but many of the normal modes of the CF_3 group are not well characterized. A number of studies on the CF_3 motions have been undertaken recently by Berney[2,3], Loos[4], and Pace[5], but assignment of many of the modes is still quite uncertain. The assignment of the CF_3 deformation and rocking modes of $(CF_3)_2O_2$ was expected to better define the frequency regions to be expected for these normal modes.

EXPERIMENTAL

The infrared spectrum of $(CF_3)_2O_2$ was recorded from 3000 to 250 cm^{-1} with a Perkin-Elmer model 521 spectrophotometer. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry nitrogen. In the high frequency region, the instrument was calibrated in the usual manner[6] while the lower region was calibrated by using atmospheric water vapor and the assignments of Randall *et al.*[7] The spectrum was recorded with the sample in a 10 cm gas-cell equipped with CsBr optics at pressures of 30, 20, and 2 torr. The matrix isolation study in the region of the CF_3 stretching modes was done at ∿20°K with an Air Products Cryotip described by White and Mann.[8] The spectrum represents 1.06 μ moles of sample in a 500:1 ratio of Ar to $(CF_3)_2O_2$.

The far infrared spectrum was recorded from 33 to 500 cm^{-1} with a Beckman Model IR-11 Spectrophotometer. The instrument housing was purged with dry air and calibrated using water vapor and the assignments of Randall *et al.*[7] All reported frequencies are expected to be accurate to better than ± 2 cm^{-1}. The cell used was a Beckman variable path length cell equipped with polyethylene windows but only a length of 8.2 m was used. Pressures were varied from 50 to 350 mm of Hg.

The Raman spectrum of the liquid was recorded with a Cary Model 81 Raman Spectrophotometer which had a circulating filter solution of 125 ml of orthonitrotoluene and 1.75 g of ethyl violet in 3 liters of isopropanol to isolate the 4358 Å mercury excitation line. Depolarization values were measured by the method of Crawford and Horwitz.[9] The Raman spectrum was recorded on 5 ml of the liquid at -80°C in a Raman tube which was cooled by a stream of gaseous N_2 precooled in a bath of liquid N_2.

RESULTS AND DISCUSSIONS

Bis(trifluoromethyl)peroxide could theoretically have any of several configurations. If the trifluoromethyl groups were cis to one another, the molecule could be classified C_{2v}, but if the two CF_3 groups were trans, one might consider the molecule as having C_{2h} symmetry. Both of these possibilities, however, seem remote in the light of the fact that both H_2O_2 and F_2O_2 possess only C_2 symmetry. If the trifluoromethyl groups were freely rotating so that they could be considered as having spherical symmetry, or if the fluorines were situated correctly, then the molecule would have a two-fold axis of symmetry and the normal modes could be described in terms of the C_2 point group and belong to the irreducible representations 13A + 11B. Consequently, in this case, a maximum of thirteen lines could be polarized in the Raman effect. If, on the other hand, the barrier to internal rotation were sufficiently high to "freeze" the trifluoromethyl groups in a staggered conformation, the molecule would possess no symmetry and belong to the C_1 species in which case all twenty-four normal modes could be polarized in the Raman spectrum. Table 1 shows that many infrared active modes are also active in the Raman effect and hence C_{2h} symmetry may be ruled out. There are also at least nine polarized bands in the Raman spectrum and hence the possibility of C_{2v} symmetry may also be precluded. Unfortunately, too few lines were observed in the Raman effect of $(CF_3)_2O_2$ to allow a definite decision as to whether the molecule had C_2 or simply C_1 symmetry. However, the appearance of two depolarized Raman lines suggests C_2 symmetry, but it must be kept in mind that polarized Raman lines can have depolarization values indistinguishable from 6/7. Regardless of the symmetry, the twenty-four fundamental vibrations arise from six skeletal motions and eighteen modes of the CF_3 group. The skeletal modes may be approximately described as one O-O and two C-O stretching vibrations, two C-O-O-C bending motions and an O-O torsional oscillation. For purposes of discussion, we shall describe the CF_3 motions by assuming first that the molecule has C_2 symmetry, i.e. the CF_3 groups are equivalent, and second that the CF_3 motions may be related to the corresponding motions of the X-CF_3 molecule with C_{3v} symmetry. Thus, when we designate symmetric and antisymmetric CF_3 modes, we will be referring to the modes which are of the A and E species of the C_{3v} point group, respectively. The CF_3 motions may be described as six stretching modes, six deformations, four rocking fundamentals and two CF_3 torsional oscillations.

Berney, *et al.*[2,3] have shown that the CF_3 stretching fundamentals lie in the frequency range of 1100-1400 cm^{-1}, and that they absorb very strongly in the infrared spectrum but weakly in the Raman effect. Figure 1 shows the infrared spectrum of gaseous $(CF_3)_2O_2$ in the spectral region 3000-250 cm^{-1}. Due to the strength of the absorptions in the 1100-1400 cm^{-1} frequency range, the spectrum of the matrix isolated molecule was studied in this region to better resolve the band centers. An X-CF_3 molecule would be expected to have a degenerate pair of CF_3 stretching modes at a higher frequency than the single symmetric CF_3 stretching fundamental. Thus, if the two motions of the two CF_3 groups in $(CF_3)_2O_2$ couple with one another and the lowering of symmetry to C_2 is sufficient to split the degenerate pair, one would expect to see four antisymmetric modes on the high frequency side of this region and two symmetric CF_3 stretching fundamentals on the low frequency side. The gas phase spectrum of $(CF_3)_2O_2$ displays seven bands in this region which can be considered as fundamentals; two on the low frequency side at 1125 cm^{-1} and 1166 cm^{-1} and five on the high frequency side at 1191 cm^{-1}, 1240 cm^{-1}, 1265 cm^{-1}, 1287 cm^{-1}, and 1320 cm^{-1}. Two of the seven bands, 1125 cm^{-1} and 1320 cm^{-1}, appear to be rather weak, and it is assumed that one of these bands is not a fundamental. On the basis of the expected appearance of this region of the spectrum, we tentatively assign the 1320 cm^{-1} absorption to a combination band and the 1125 cm^{-1} band to a symmetric CF_3 stretching mode. Thus, the two symmetric CF_3 stretching fundamentals absorb at 1125 cm^{-1} and 1166 cm^{-1} while the antisymmetric CF_3 stretching modes lie at 1191 cm^{-1}, 1240 cm^{-1}, 1265 cm^{-1}, and 1287 cm^{-1}. The CF_3 stretching modes appear in the Raman effect of $(CF_3)_2O_2$ (fig. 2) as one weak and very asymmetric band at 1244 cm^{-1}, consequently, no quantitative depolarization values could be obtained to substantiate our assignments.

Arvia and Aymonino[1] have assigned the two C-O stretching modes to a weak band at 974 cm^{-1} and a medium intensity band at 886 cm^{-1}. The antisymmetric stretching vibration is expected to fall at the higher frequency and to be the band of stronger intensity in the infrared spectrum, in contradiction to their assignments. They place the O-O stretching mode at 821 cm^{-1}. These assignments, however, are not consistent with the Raman data obtained in this study. The O-O stretching mode is expected to be weak in the infrared spectrum, but it is also expected to be the strongest band in the Raman spectrum. The Raman spectrum of bis(trifluoromethyl)peroxide shows only two bands in this region of the spectrum, a very intense, polarized band at 886 cm^{-1} and another strong, polarized band at 967 cm^{-1}. The 886 cm^{-1} band is twice as intense as any other band in the spectrum and is confidently assigned to the O-O stretching mode. Since the symmetric C-O stretching fundamental is expected to be weak in the infrared spectrum but strong in the Raman effect, the 975 cm^{-1} infrared absorption may be assigned to the symmetric

C-O stretching vibration, the antisymmetric C-O stretching fundamental, on the other hand, is expected to be weak in the Raman effect and strong in the infrared spectrum. Thus, we have assigned the antisymmetric C-O stretching mode to the infrared band at 1065 cm^{-1}. No Raman counterpart was observed.

Berney[3] assigns the CF_3 deformations in hexafluoroacetone to the frequency range of 718 cm^{-1} to 506 cm^{-1}. Loos[4] places the deformations for a series of molecules with the CF_3 group in a range of frequencies from 832 cm^{-1} to 540 cm^{-1}. Bis(trifluoromethyl)peroxide has six fundamental modes which may be described as CF_3 deformations, and six bands are found in the expected frequency range of the infrared spectrum. Thus, we assign the six bands at 713 cm^{-1}, 673 cm^{-1}, 634 cm^{-1}, 627 cm^{-1}, 610 cm^{-1}, and 558 cm^{-1} to the CF_3 deformation modes. Only three of these bands were observed in the Raman spectrum of $(CF_3)_2O_2$ — a strong band at 706 cm^{-1} which was strongly polarized and two depolarized bands at 605 cm^{-1} and 558 cm^{-1}. Thus, the 706 cm^{-1} band must arise from the symmetric CF_3 deformation and belong to the A irreducible representation of the C_2 point group. There should be two symmetric CF_3 deformations and four antisymmetric deformations, and since the 713 cm^{-1} is definitely a symmetric mode, there is no reason to believe that the other symmetric mode will not also lie on the high frequency side of this region. Therefore, the infrared bands at 713 cm^{-1} and 673 cm^{-1} are assigned as the symmetric CF_3 deformations while the bands at 634 cm^{-1}, 627 cm^{-1}, 610 cm^{-1}, and 558 cm^{-1} are assigned to the antisymmetric CF_3 deformational modes.

Assignment of the CF_3 rocking modes and skeletal bending vibrations is considerably more difficult. No previous study of the C-O-O-C skeletal bending modes has been made, and frequencies for CF_3 rocking fundamentals range from 464 cm^{-1} for CF_3-C≡C-CF_3[2] to as low as 155 cm^{-1} for $CF_3N=CF_2$[4]. In the study of $(CF_3)_2S_2$[4], a band at 339 cm^{-1} was observed in the Raman spectrum but not in the infrared spectrum and was assigned as a CF_3 rocking mode. This datum is in excellent agreement with a band we observe at 340 cm^{-1} in the Raman spectrum of $(CF_3)_2O_2$, and, consequently, it is assigned to one of the four rocking fundamentals. Unfortunately, the similarity of the two spectra stops here. The bands which seem most difficult to assign are the two bands at 490 cm^{-1} and 445 cm^{-1} in the infrared spectrum of the peroxide (the 445 cm^{-1} band appears as a very pronounced shoulder in the far infrared spectrum which is not reproduced here), with corresponding Raman lines at 488 cm^{-1} and 439 cm^{-1}. On the basis of previous work, these frequencies would appear to be too high to be assigned to CF_3 rocking modes. However, they are too strong to be combination or overtone bands and are much too high in frequency to be considered as due to the skeletal bending modes. Thus, we are left little choice but to assign these bands as CF_3 rocking fundamentals. The far infrared spectrum of bis(trifluoromethyl)peroxide (Fig. 3) displays a strong band centered at 215 cm^{-1}. In the Raman effect of this molecule, however, this band is seen to split into two bands, a strong, polarized band at 228 cm^{-1} and a weaker band at 211 cm^{-1}. Due to the relative intensities of these bands, we have tentatively assigned the 211 cm^{-1} band to the fourth CF_3 rocking mode while the 228 cm^{-1} absorption has been ascribed to a C-O-O-C bending motion.

Below 150 cm^{-1} in the infrared spectrum of $(CF_3)_2O_2$, we have observed three bands which must be assigned to a C-O-O-C bending mode, a torsional oscillation about the O-O bond, and the two CF_3 torsional modes. These bands are all extremely weak, for the pressure distance product is 4 meter atmospheres. The strongest band in this portion of the infrared spectrum is found at 134 cm^{-1} and since in general bending modes absorb more strongly and at a higher frequency than do torsional modes, we have assigned the 134 cm^{-1} band to the other C-O-O-C bending mode. There is some doubt as to the actual shape of the next band observed, at 94 cm^{-1}, for it occurs at a grating change and there is some pen drift after the change. However, we have tentatively assigned this band to the O-O torsional mode. This frequency does compare well with the S-S torsional vibration in $(CF_3)_2S_2$[4] which has been assigned to a band at 80 cm^{-1}. The extremely weak band at 64 cm^{-1} must then be assigned to the CF_3 torsional modes. Again, this frequency is in good agreement with other CF_3 torsions which range from 50 cm^{-1} in CF_3CFO[4] and $(CF_3)_2CO$ to 66 cm^{-1} in $(CF_3)_2CO$[3] with several falling at about 60 cm^{-1}.

The determination of torsional barriers from the frequency of the 1←0 transition has been discussed previously,[10,11,12] and only a review of the calculations is presented here. The frequency of the 1←0 transition may be expressed as

$$\bar{\nu} = \left(\frac{n}{2}\right)^2 F(\Delta b_{v\sigma}) \qquad (1)$$

where n is the number of barriers, F is the reduced moment constant and $\Delta b_{v\sigma}$ is the difference between the Mathieu eigenvalues of the v=0 and v=1 states. Thus, if F can be determined and the frequency of the fundamental is known, $\Delta b_{v\sigma}$ can be calculated. From this value of $\Delta b_{v\sigma}$, a parameter s may be obtained from tables of Mathieu equation solutions. The barrier height of the torsion may then be calculated by

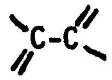
$$V_n = \left(\frac{n}{2}\right)^2 Fs. \qquad (2)$$

Alternately, the torsional oscillation may be assumed to be harmonic in the region of the first transition. Fateley et al.[13] have shown that the result of this approximation is

$$V_1 + 4V_2 + 9V_3 = \frac{\bar{\nu}^2}{F} \qquad (3)$$

It must be remembered that inherent in all of these calculations is the assumption that $\bar{\nu}$ is the frequency of the "pure" torsional oscillation. In the case of the CF_3 torsions, the assumption would appear more reasonable than for the 0-0 torsion which is almost certainly coupled to the bending modes. Thus, the following calculations must be viewed as upper limits for the barriers.

In order to calculate the various moments of inertia required in the determination of F, it was necessary to estimate the molecular parameters of $(CF_3)_2O_2$; the most uncertain of which is the dihedral angle between the two COO planes which was assumed to be 90°. The results were F values of 0.244 cm^{-1} about the C-0 bonds and 1.12 cm^{-1} about the 0-0 bond. The calculations of the height of the three-fold barrier restricting internal rotation of the two CF_3 groups was done via equations 1 and 2 and the tables of Fateley, Miller, and Witkowski.[12] Thus, the 64 cm^{-1} absorption yielded a value of 1897 cm^{-1} or 5.42 kcal/mole for the upper limit of the three-fold barrier. It is interesting to note that the alternate method gave values which differed from the above by less than 2%. This barrier appears to be very high when compared with other CF_3 barriers, e.g. 1.4 kcal/mole for CF_3CFO, 2.9 kcal/mole for CF_3SCl, and 3.3 kcal/mole for $CF_3N = CF_2$ which were all done by Loos.[4] Thus, the large value of the barrier indicates that the CF_3 torsion couples with other modes or that the F value is incorrect.

In the case of the 0-0 torsion, no meaningful barrier can be calculated with only one piece of experimental datum because the potential will consist of two unequal barriers at the trans and cis conformations ($V_{cis} >> V_{trans}$). What has been attempted is a semi-quantitative discussion of the range in which the barrier heights are likely to fall. If we assume that the barrier to internal rotation is due only to the steric effects of the two CF_3 rotors, the most stable conformation would be trans, and the potential would consist of a single barrier. The s value for this case is about 23,000 which is so large as to make its exact value unobtainable, consequently, the second method was employed. Thus, from equation 3, $V_1 = \bar{\nu}^2/F$ ($V_2 = V_3 = 0$) so that an absorption of 94 cm^{-1} for $(CF_3)_2O_2$ gives a one-fold barrier height of 7,857 cm^{-1} or 22.5 kcal/mole which is expected to be the upper limit of the cis barrier. The barrier will also be due to the strong interaction of the two pairs of electrons in the cis and trans postions. Thus, we may obtain the lower limit for the cis barrier by neglecting the steric effects of the CF_3 groups and by assuming a simple two-fold barrier, i.e. $V_{trans} = V_{cis}$. From equation 3, it can be seen that $V_2 = \bar{\nu}^2/4F$ ($V_1 = V_3 = 0$). Thus, the result of 1964 cm^{-1} = 5.61 kcal/mole is expected to be the lower limit of the cis barrier and the upper limit of the trans barrier. The Mathieu eigenvalue leads to a barrier of 2012 cm^{-1} or 5.75 kcal/mole. Hunt et al.[14] have found that for hydrogen peroxide V_{trans} = 386 cm^{-1} while V_{cis} = 2460 cm^{-1}. If the trans barriers of both H_2O_2 and $(CF_3)_2O_2$ arise mainly from interaction of the two pairs of non-bonded electrons, one would not expect the two trans barriers to be too different. Thus, V_2 = 1964 cm^{-1} is too high for the trans barrier, and it must be too low for the cis barrier. It is also believed that 7,857 cm^{-1} is the upper limit of the cis barrier, but it is expected to be greater than 2460 cm^{-1}, the H_2O_2 cis barrier. Consequently, we feel that the cis barrier height is in the range of 16 ± 6 kcal/mole which is comparable to the barriers found by Fateley et al.[13] for C-C torsions in molecules with a  structure.

SUMMARY

Table II gives a summary of the assignments of the twenty-four fundamental modes of bis(trifluoromethyl)peroxide. The number of polarized lines in the Raman spectrum implies that the molecule cannot have C_{2h} or C_{2v} symmetry, and thus must possess either C_2 or C_1 symmetry. The two CF_3 torsions have been assigned to a band at 64 cm^{-1} which yields a barrier to internal rotation of about 5.4 kcal/mole. The O-O torsion has been assigned to a band at 94 cm^{-1}, but only a semi-quantitative discussion of the barrier could be given.

ACKNOWLEDGEMENT

The authors wish to acknowledge Dr. Fateley for the calculations of reduced moments of inertia and the National Aeronautics and Space Administration for financial support given through Grant NGR-41-002-003[illegible].

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Table I. Infrared and Raman Frequencies of Bis(trifluoromethyl)peroxide.

INFRARED(gas)		RAMAN (liquid at -80°C)			
$\tilde{\nu}$(cm^{-1})	Relative Intensity	$\Delta\bar{\nu}$	Relative Intensity	Depolarization Values	Assignments*
64	vvw				ν_{13}, ν_{24}
94	vw				ν_{12}
134	w				ν_{23}
215	m	211	7	0.4	ν_{11}
		228	25	0.45	ν_{10}
		340	25	0.63	ν_{22}
445	sh	439	7	0.2	ν_9
490	m	488	5	0.6	ν_{21}
558	w	558	16	6/7 dp	ν_{20}
610	sh	605	14	6/7 dp	ν_{19}
627	s				ν_8
634	sh				ν_7
673	w				ν_{18}
713	m	706	30	0.31	ν_6
890	m	886	100	0.22	ν_5
936^+					—
975	w	967	40	0.65	ν_4
1065	m				ν_{17}
1125	s				ν_3
1166	vvs				ν_{16}
1191	sh				ν_2
1240	vs	1244	11	0.53	ν_1
1265	vs				ν_{15}
1287	vs				ν_{14}

Table I. (continued)

INFRARED (gas)		RAMAN (liquid at -80°C)			
$\tilde{\nu}(\mathrm{cm}^{-1})$	Relative Intensity	$\Delta\tilde{\nu}$	Relative Intensity	Depolarization Values	Assignments*
1320	sh				$\nu_2 + \nu_{23} = 1325$; $\nu_6 + \nu_{19} = 1323$
1378	m				$\nu_5 + \nu_{21} = 1375$
1394	m				$\nu_{14} + \nu_{23} = 1399$
1452	m				$\nu_5 + \nu_{20} = 1448$; $\nu_4 + \nu_{21} = 1460$
1511	m				$\nu_{17} + \nu_9 = 1510$; $\nu_5 + \nu_8 = 1517$
1502	m				$\nu_{16} + \nu_{22} = 1506$; $\nu_{19} + \nu_5 = 1500$
1600	m				$\nu_4 + \nu_8 = 1602$; $\nu_5 + \nu_6 = 1603$
1991	w				$\nu_{14} + \nu_6 = 2000$
2053	w				$\nu_{16} + \nu_5 = 2056$
2137	m				$\nu_{16} + \nu_4 = 2141$
2408	w				$\nu_{14} + \nu_3 = 2412$; $\nu_1 + \nu_{16} = 2406$
2488	w				$2\nu_1 = 2480$
2536	m				$2\nu_{15} = 2530$

Abbreviations used are v, w, m, s, sh and dp meaning very, weak, medium, strong, shoulder, and depolarized, respectively.

* The numbering system used implys a C_2 symmetry, and in many cases the choice of A or B mode is arbitrary.

\+ The relative intensity of this band changes over a period of several days and it is assumed to be due to an impurity.

Table II. Summary of the Fundamentals[+]

A Species

$\bar{\nu}$ (cm^{-1})	Assignment	Description
1240	ν_1	antisymmetric CF_3 stretching
1191	ν_2	sntisymmetric CF_3 stretching
1125	ν_3	symmetric CF_3 stretching
975	ν_4	symmetric C-O stretching
890	ν_5	O-O stretching
713	ν_6	symmetric CF_3 deformation
634	ν_7	antisymmetric CF_3 deformation
627	ν_8	antisymmetric CF_3 deformation
445	ν_9	CF_3 rocking
228*	ν_{10}	C-O-O-C bending
211*	ν_{11}	CF_3 rocking
94	ν_{12}	O-O torsion
64	ν_{13}	CF_3 torsion

B Species

$\bar{\nu}$ (cm^{-1})	Assignment	Description
1287	ν_{14}	antisymmetric CF_3 stretching
1265	ν_{15}	antisymmetric CF_3 stretching
1166	ν_{16}	symmetric CF_3 stretching
1065	ν_{17}	antisymmetric C-O stretching
673	ν_{18}	symmetric CF_3 deformation
610	ν_{19}	antisymmetric CF_3 deformation
558	ν_{20}	antisymmetric CF_3 deformation
490	ν_{21}	antisymmetric CF_3 rocking
340*	ν_{22}	CF_3 rocking
134	ν_{23}	C-O-O-C bending
64	ν_{24}	CF_3 torsion

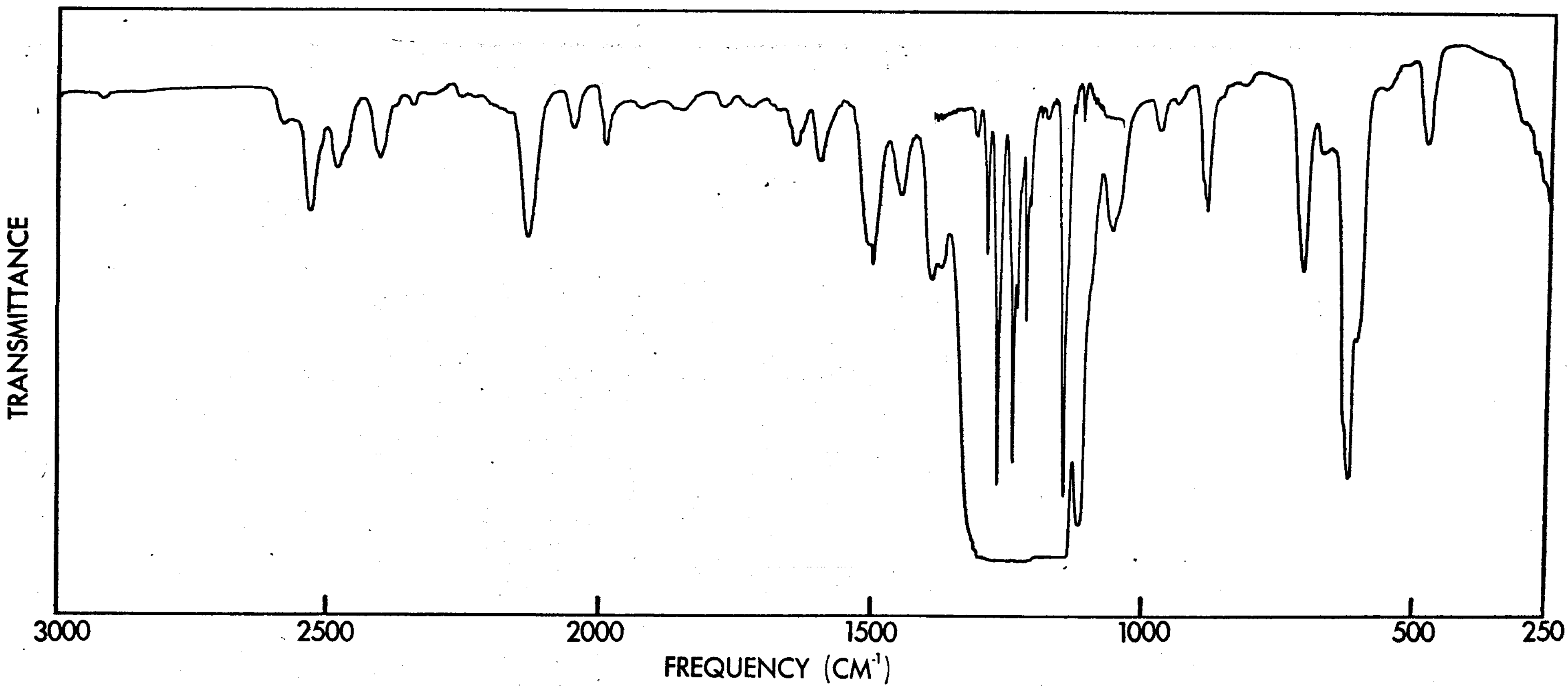
* Raman frequencies, all others are infrared frequencies.

List of Figures

Figure 1. The infrared spectrum of 30 torr of $(CF_3)_2O_2$ recorded in a 10 cm cell with CsBr windows. The inlay is from the spectrum of 1.06 μ moles of sample in a 500:1 mole ratio $[Ar:(CF_3)_2O_2]$ at 20°K.

Figure 2. Raman spectrum of 5 ml of liquid $(CF_3)_2O_2$ at -80°C.

Figure 3. The far infrared spectrum of $(CF_3)_2O_2$ recorded with an 8.2 m path length. The pressures used were 50 torr from 150 to 300 cm^{-1} and 350 torr from 33 to 150 cm^{-1}.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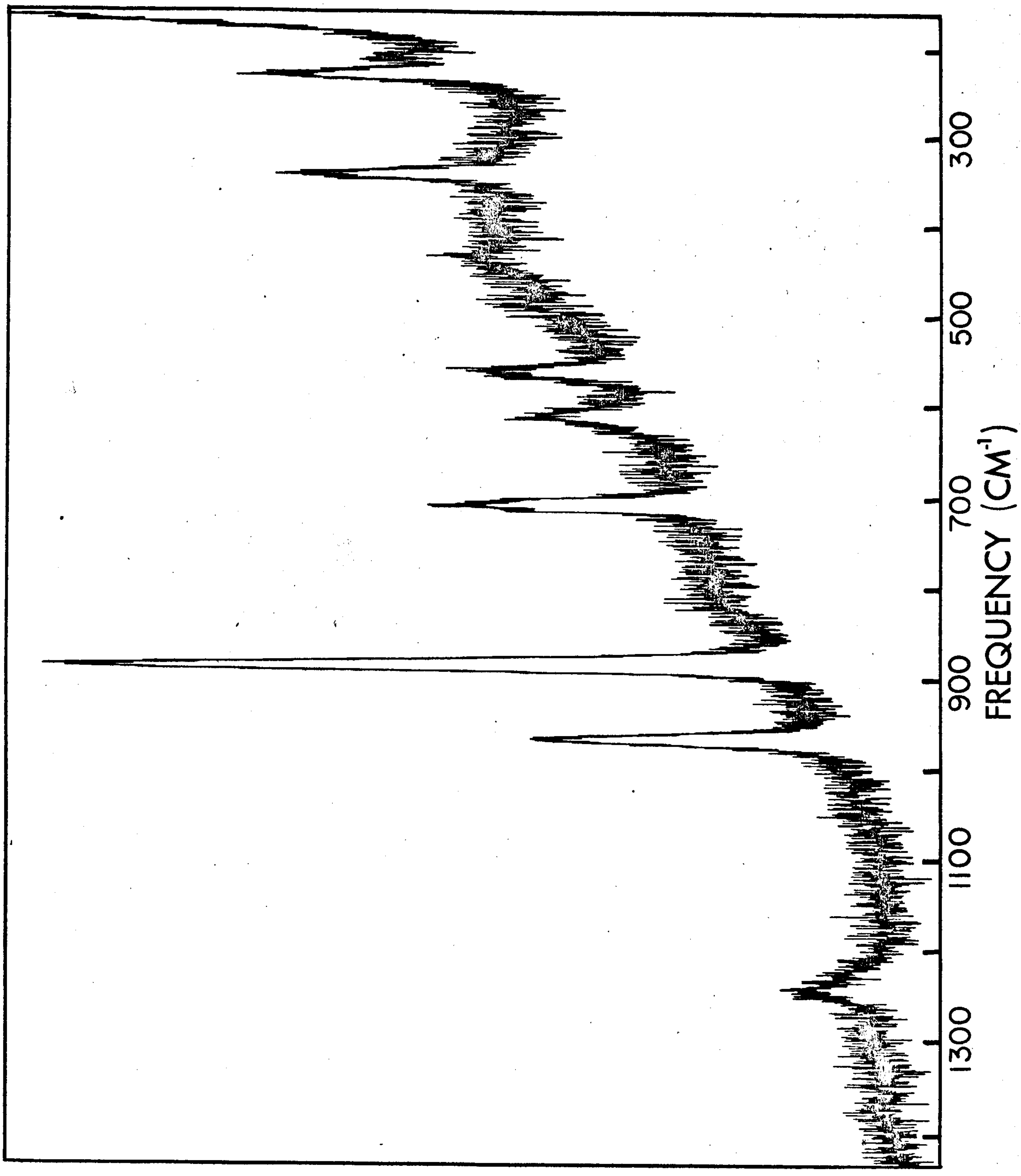
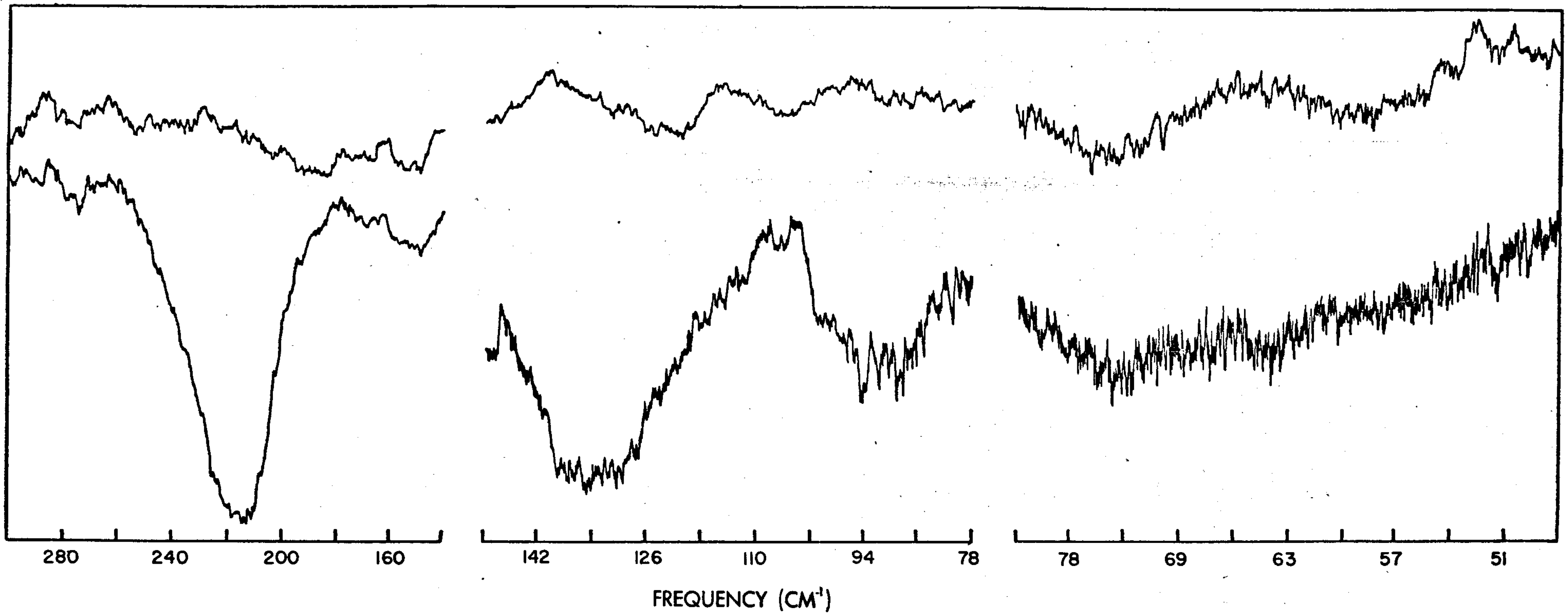

300
500
700
900
1100
1300
FREQUENCY (CM^{-1})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240
200
160
142
126
110
94
78
78
69
63
57
51
FREQUENCY (CM⁻¹)