

## INFRARED SPECTRA OF HEPTAFLUOROBUTYRIC ACID AND SOME OF ITS ESTERS

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(Received August 21, 1972)

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### SUMMARY

Infrared spectra obtained for seven alkyl esters of heptafluorobutyric acid show that 18 vibrations of the  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2$  group have characteristic frequencies in these esters, with most having average deviations of only about  $1\text{ cm}^{-1}$ . The relative intensities of the bands are also quite constant. The infrared spectrum obtained for heptafluorobutyric acid indicates that the acid is completely associated in the neat liquid.

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### INTRODUCTION

Infrared spectra have recently been presented for several trifluoroacetate esters<sup>1-3</sup>, pentafluoropropionic acid<sup>4</sup> and several pentafluoropropionate esters<sup>5</sup>. A number of vibrations were shown to be characteristic of each of the  $\text{CF}_3\text{CO}_2$  and  $\text{CF}_3\text{CF}_2\text{CO}_2$  groups in the two ester families, and in general there is good agreement between the frequencies of the corresponding vibrations of trifluoroacetate and pentafluoropropionate esters. This work has now been extended to include heptafluorobutyric acid and seven esters of this acid. Included in the study are the methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl and n-pentyl esters.

### EXPERIMENTAL

The infrared spectra were obtained with a Beckman IR-12 spectrophotometer. The esters were all prepared from the acid and corresponding alcohol. The spectra showed essentially that no starting material was present.

### RESULTS AND DISCUSSION

The  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2$  group has 13 atoms and therefore has 12 stretching, 18 angle-bending and three torsional modes. The torsions and about half the angle-

bending vibrations will have frequencies that lie below the region investigated, which was  $4000\text{--}400\text{ cm}^{-1}$ . Therefore, we would expect to observe bands for approximately 20–25 fundamentals of the heptafluorobutyrate group.

#### *Heptafluorobutyric acid*

The infrared spectrum of heptafluorobutyric acid is shown in Figure 1 for the neat liquid. The spectrum shows the acid to be completely associated in the liquid state, as is demonstrated by the absence of the monomeric  $\text{C}=\text{O}$  stretch at about  $1820\text{ cm}^{-1}$  and the  $\text{O-H}$  stretch at about  $3580\text{ cm}^{-1}$  (this latter region is not shown in the figure). The monomeric  $\text{O-H}$  stretching frequency has been reported at  $3581\text{ cm}^{-1}$  for the vapor<sup>6</sup>, the same as for  $\text{C}_2\text{F}_5\text{COOH}$ . The broad  $\text{O-H}$  absorption centered at about  $3180\text{ cm}^{-1}$  is indicative of the hydrogen bonding present in the acid, and this frequency is slightly higher than for the associated form of trifluoroacetic acid ( $3134\text{ cm}^{-1}$ )<sup>7</sup> and pentafluoropropionic acid ( $3150\text{ cm}^{-1}$ )<sup>4</sup>. The dimer  $\text{C}=\text{O}$  and  $\text{C-O}$  stretching frequencies,  $\text{O-H}$  bend and  $\text{CO}_2$  bend are about the same as for  $\text{C}_2\text{F}_5\text{COOH}$ .

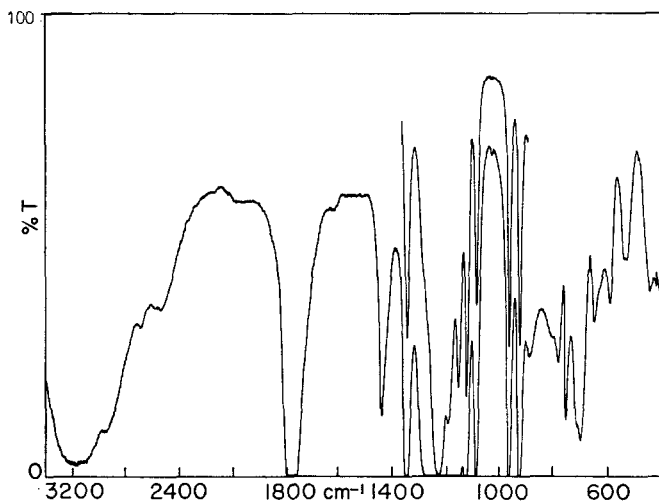


Fig. 1. Infrared spectrum of heptafluorobutyric acid liquid. Path length; 0.015 mm or film.

The bands observed in the region  $800\text{--}1400\text{ cm}^{-1}$  can be due only to the  $\text{C-F}$  and  $\text{C-C}$  stretching vibrations and  $\text{C-O-H}$  bend. The  $\text{C-O}$  stretch can be assigned to the band observed at  $1450\text{ cm}^{-1}$ , which is the same as for  $\text{C}_2\text{F}_5\text{COOH}$ .

#### *Heptafluorobutyrate esters*

Liquid-state infrared spectra for the seven esters listed in the introductory section are shown for the region  $400\text{--}3200\text{ cm}^{-1}$  in Figures 2–8, and the frequencies that seem to be characteristic of the perfluorobutyrate group are listed in Table 1.

TABLE 1  
CHARACTERISTIC WAVE NUMBERS (cm<sup>-1</sup>) IN CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>COOR ESTERS

R =	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	n-C <sub>3</sub> H <sub>7</sub>	i-C <sub>3</sub> H <sub>7</sub>	n-C <sub>4</sub> H <sub>9</sub>	i-C <sub>4</sub> H <sub>9</sub>	n-C <sub>5</sub> H <sub>11</sub>	Average
	1788	1785	1785	1780	1784	1780	1787	1784±2
	1311	1309	1307	1307	1307	1308	1307	1308±1
	1272	1268	1272	1272	1271	1269	1271	1271±1
	1226 <sup>a</sup>	1232	1233	1232	1232	1231	1232	1232±1
		1224	1220	1224	1221	1221	1220	1222±1
	1192	1193	1192	1192	1194	1194	1193	1193±1
	1147	1148	1147	1155	1148	1155	1148	1150±3
	1126	1127	1125	1127	1127	1127	1125	1126±1
	1088	1085	1086	1087	1088	1085	1087	1087±1
	981	969	973	973	972	971	973	973±2
	926	936	947	941	~940	941	940	939±4
	759	759	759	759	760	759	758	759±1
	745	744	744	745	745	744	744	744±1
	723	722	722	721	722	720	722	722±1
	649	649	~650	646	650	646	648	648±1
	591	590	592	590	593	590	591	591±1
	534	535	531	531	533	530	530	532±2
	419	421	421	420	?	421	419	420±1

<sup>a</sup> Two unresolved bands.

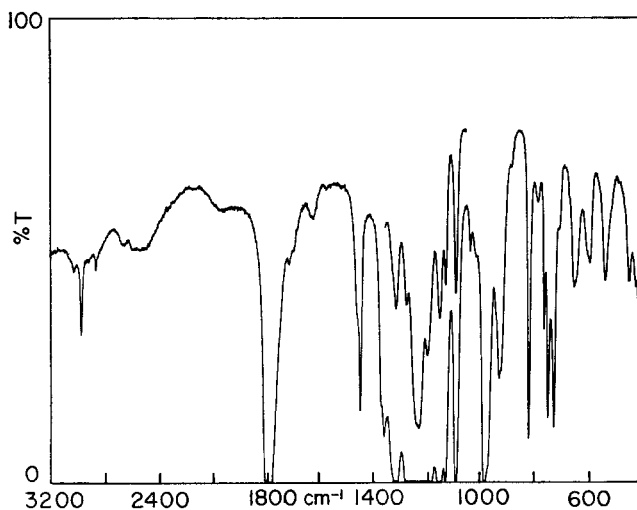


Fig. 2. Infrared spectrum of methyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

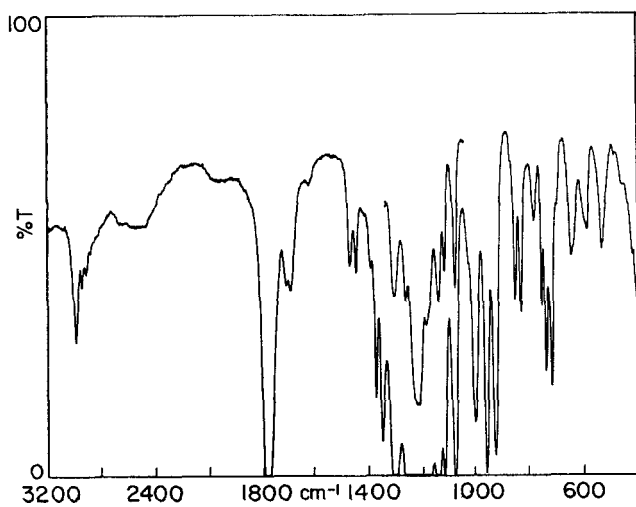


Fig. 3. Infrared spectrum of ethyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

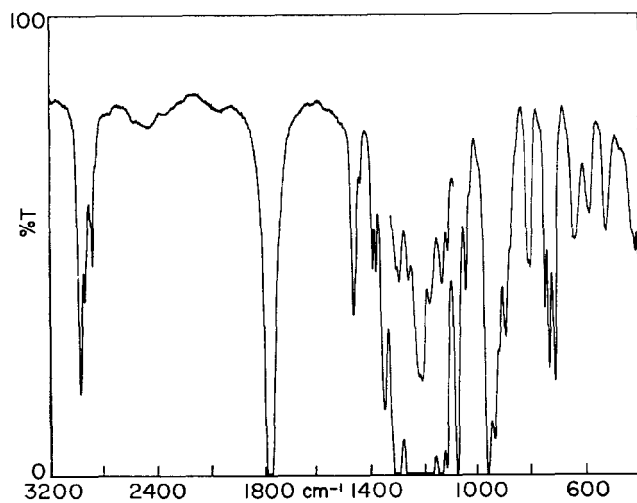


Fig. 4. Infrared spectrum of n-propyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

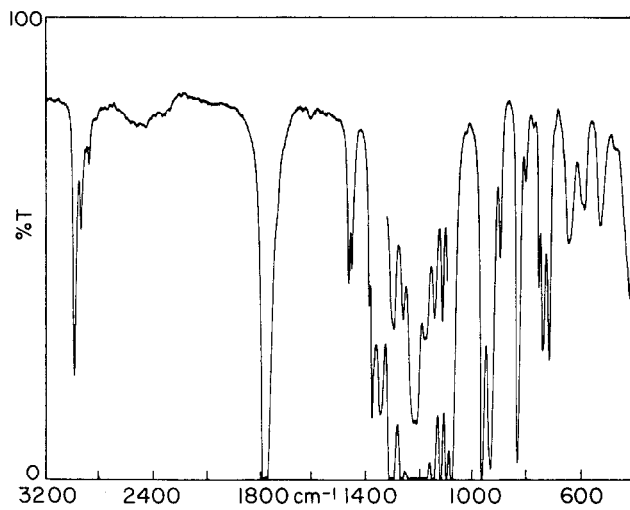


Fig. 5. Infrared spectrum of *i*-propyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

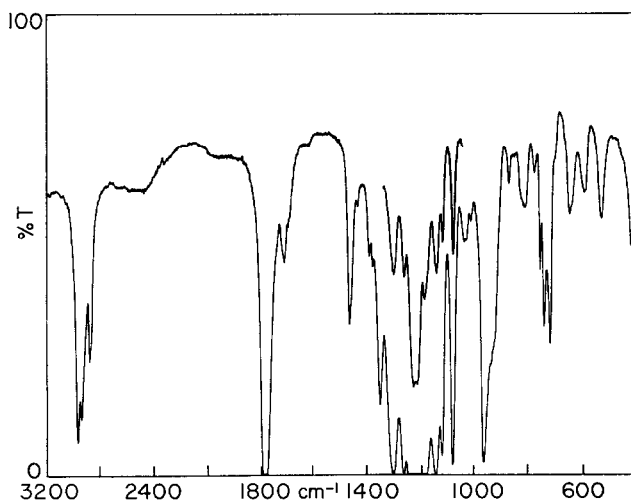


Fig. 6. Infrared spectrum of *n*-butyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

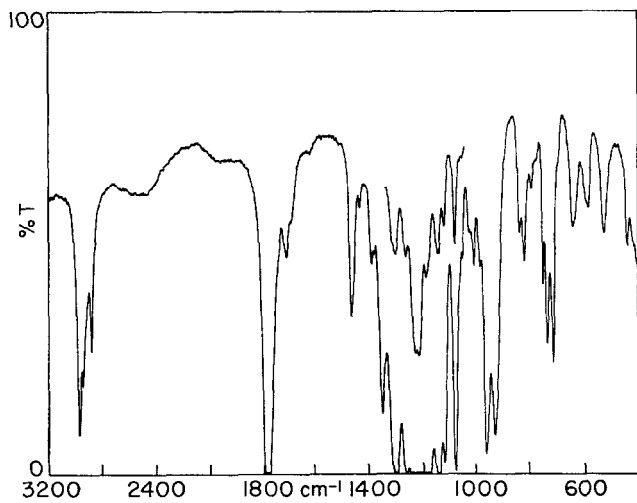


Fig. 7. Infrared spectrum of *i*-butyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

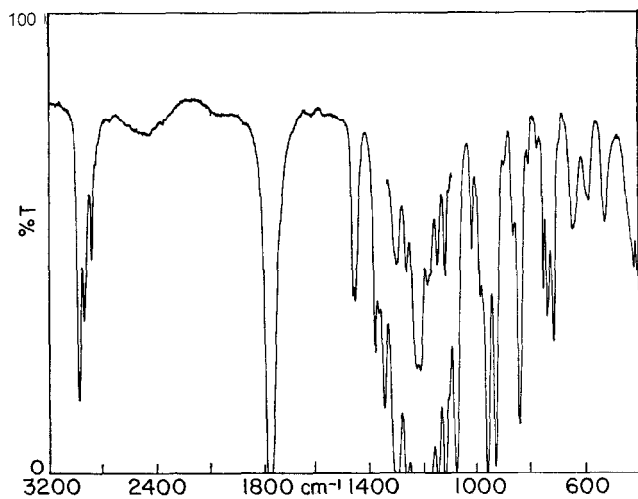


Fig. 8. Infrared spectrum of *n*-pentyl heptafluorobutyrate liquid. Path length: 0.015 mm or film.

*Vibrational assignments**Carbonyl stretching frequencies*

The average value for the  $C=O$  stretching frequency of the perfluorobutyrate (PFB),  $1784\text{ cm}^{-1}$ , is exactly the same as the average value for the perfluoropropionate (PFP) but lower than for the trifluoroacetate (TFA). Changing the group bonded to  $COOR$  from  $CF_3$  to  $CF_3CF_2$  lowers the carbonyl frequency because of the decrease in the electronegativity of the bonded group ( $CF_3 > C_2F_5$ )<sup>4</sup>. However, the  $C_3F_7$  group should have essentially the same electronegativity as  $C_2F_5$  and exchanging these groups does not affect the carbonyl stretching frequency.

The monomeric acid carbonyl stretching frequency is higher than that of any of the esters. Although the monomer does not exist in the neat liquid to an appreciable extent, the value in solution in non-polar solvents is about  $1810\text{ cm}^{-1}$ <sup>6</sup>.

*Carbon-carbon and carbon-fluorine stretching frequencies*

The only vibrations of the  $C_3F_7CO_2$  group that will have frequencies in the  $800\text{--}1500\text{ cm}^{-1}$  region are the  $C-F$ ,  $C-C$  and  $C-O$  stretches. However, this region will be complicated by the presence of bands due to  $C-C$  and  $O-C$  stretches and carbon-hydrogen bending vibrations of the alkyl groups, with the number of bands being dependent on the complexity of the group bonded to the oxygen.

The two highest-frequency bands listed in Table 1 for this region can be assigned to  $C-C$  stretching vibrations. Assignment of these relatively high frequencies to  $C-C$  stretches has been supported by normal coordinate calculations of fluorinated compounds, a number of which have been discussed by Tuazon, Fateley and Bentley<sup>8</sup>. Thus, for example, the  $C-C$  stretch in  $CF_3CH_3$  is  $9\ 1280\text{ cm}^{-1}$ .

The most intense bands in the spectrum, barely resolved at  $1232$  and  $1222\text{ cm}^{-1}$ , can undoubtedly be assigned to  $C-F$  asymmetric stretches (probably of the  $CF_3$  group) and those of the  $CF_2$  groups should lie between  $1100$  and  $1200\text{ cm}^{-1}$ . The other  $C-C$  stretch band should be either the  $973$  or  $939\text{ cm}^{-1}$  band with the other one of this pair assignable to a  $C-F$  symmetric stretch. Actually, the  $C-F$  and  $C-C$  stretching modes will be highly mixed insofar as the symmetry of the molecule permits, and the bands in the region  $900\text{--}1300\text{ cm}^{-1}$  should be considered to be due to such mixtures.

There are nine bands listed in Table 1 for the  $800\text{--}1320\text{ cm}^{-1}$  region, and there should be 11 stretching vibrations in this region. There are one or more bands in the  $800\text{--}850\text{ cm}^{-1}$  region of the spectrum for each compound but the position and intensity of this band varies more than for any of the others listed. For this reason this band was not included in Table 1, especially since it would be difficult to choose between bands only *ca.*  $20\text{ cm}^{-1}$  apart in this region. However, it is likely that one of the  $C-F$  symmetric stretching bands lies in this region, as was assigned for PFP and TFA. If this assignment is made, the only stretching band not assigned for the  $C_3F_7CO_2$  group is the  $C-O$  stretch.

*Bending vibrations*

Seven frequencies listed in Table 1 remain to be assigned, all to bending vibrations in the 400–800  $\text{cm}^{-1}$  region. The most definite of these are the two asymmetric  $\text{CF}_3$  deformations which may be assigned to those bands whose average values are 591 and 532  $\text{cm}^{-1}$ . These values compare very well with those of PFP, which are 595 and 544  $\text{cm}^{-1}$ , and with TFA, which are 596 and 526  $\text{cm}^{-1}$ . The  $\text{CF}_3$  symmetric deformation,  $\text{CF}_2$  bends and  $\text{O}-\text{C}=\text{O}$  bend can be assigned to the four bands in the 600–800  $\text{cm}^{-1}$  region. The lowest frequency listed, 420  $\text{cm}^{-1}$ , can be assigned to a  $\text{C}-\text{C}-\text{C}$  bend. The n-butyl ester has a band in this region at 446  $\text{cm}^{-1}$ , but the values for the other six esters show a range of only 2  $\text{cm}^{-1}$ . Therefore, it seems likely that a band at about 420  $\text{cm}^{-1}$  in this compound is too weak to show up in the KCl absorption of the cell windows, and that the 446  $\text{cm}^{-1}$  band is due to another vibration.

Not only are the frequencies listed in Table 1 for each vibration relatively constant among the seven esters, but the relative intensities of the bands are approximately constant.

## ACKNOWLEDGEMENTS

The author is grateful to The Robert A. Welch Foundation, Houston, Texas, for financial support of this work.

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